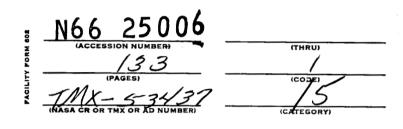
NASA TECHNICAL MEMORANDUM

NASA TM X-53437

April 18, 1966

NASA TM X-53437



THE MAKING OF TITANIUM AND TITANIUM-ALLOY SHAPES BY CASTING, POWDER METALLURGY, AND OTHER PROCESSES

By J. G. Kura, V. D. Barth, H. McCurdy, W. H. Safranek, E. T. Hall, and H. O. McIntire

Prepared Under the Supervision of the Research Branch, Redstone Scientific Information Center Directorate of Research and Development U. S. Army Missile Command Redstone Arsenal, Alabama

NASA

George C. Marshall Space Flight Center, Huntsville, Alabama

GPO PRICE \$	
CFSTI PRICE(S) \$	
Hard copy (HC)	4.00
Microfiche (MF)	1.00

653 July 65

TECHNICAL MEMORANDUM X-53437

THE MAKING OF TITANIUM AND TITANIUM-ALLOY SHAPES BY CASTING, POWDER METALLURGY, AND OTHER PROCESSES

By

J. G. Kura, V. D. Barth, H. McCurdy, W. H. Safranek, E. T. Hall, and H. O. McIntire*

ABSTRACT

25006

The state of the art of making titanium and titanium-alloy shapes by methods other than machining from wrought materials is reviewed. The methods covered are casting, powder metallurgy, metal spraying, electroforming and chemical vapor deposition. Of these methods only casting and powder metallurgy are being used to any great extent or offer a great deal of promise. Metal spraying may have some very specialized applications. In their present state of development electroforming and chemical vapor deposition are not promising methods for making titanium parts.

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

^{*}Principal Investigators, Battelle Memorial Institute, Contract No. DA-01-021-AMC-11651(Z)

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

TECHNICAL MEMORANDUM X-53437

THE MAKING OF TITANIUM AND TITANIUM-ALLOY SHAPES BY CASTING, POWDER METALLURGY, AND OTHER PROCESSES

By

J. G. Kura, V. D. Barth, H. McCurdy, W. H. Safranek, E. T. Hall, and H. O. McIntire

Prepared for

Manufacturing Engineering Laboratory

In Cooperation With

Technology Utilization Office

Under the Supervision of

Redstone Scientific Information Center
U. S. Army Missile Command
Redstone Arsenal, Alabama
MSFC Order No. H-76715
Report No. RSIC-471

Subcontracted to

Battelle Memorial Institute
505 King Avenue
Columbus, Ohio
Contract No. DA-01-021-AMC-11651(Z)

PREFACE

This report is one of a series of state-of-the-art reports being prepared by Battelle Memorial Institute, Columbus, Ohio, under Contract No. DA-01-021-AMC-11651(Z), in the general field of materials fabrication.

The making of titanium and titanium-alloy shapes by casting, powder metallurgy, and other processes is reviewed. In addition to casting and powder metallurgy, consideration was given to production of shapes by spraying, electroforming, and chemical vapor deposition. The report brings together information from a wide variety of sources for the purpose of making it available to those who can use it in industry, in the military, and in the aerospace industry.

TABLE OF CONTENTS

						Page
SUMMARY	•			•	٠	1
Castings	•					1
Powder-Metallurgy Products						1
Sprayed Bodies						3
Electroforms						3
Chemical Vapor Deposition						3
INTRODUCTION	•	•	•	•		3
SHAPING BY CASTING	•		•	•	•	4
Historical Background						4
Melting Method						5
Molding Materials						11
Impel Process						11
Oremet Practice						12
Casting Characteristics						15
Effect of Mold Materials on Properties						15
Soundness of Castings						16
Size Limitations and Casting Yield						16
Dimensional Tolerances and Finish						17
Properties of Castings						18
Future Casting Process	•	•			•	22
SHAPING BY POWDER METALLURGY	•	٠	•	٠	•	23
Powder Production				•		23
Methods of Consolidation						36
Conventional Cold Pressing			•		•	36
Sintering Temperature and Atmosphere						43
Hot Pressing and Press Forming						49
Isostatic Compaction						51
Rolling of Powder						52
High-Velocity Compaction						55
Pressureless Consolidation						56
Titanium-Base Alloys						56
Inert-Dispersoid-Strengthened Titanium .						62
Economics		•	•			62
Safety in Storage and Handling						62

TABLE OF CONTENTS (Continued)

		Page
SHAPING BY SPRAYING		. 72
Type of Equipment Required		. 75
SHAPING BY ELECTROFORMING		. 76
SHAPING BY CHEMICAL VAPOR DEPOSITION		. 77
CONCLUSIONS AND RECOMMENDATIONS	• ,	. 78
Shaping by Casting		. 79 . 79 . 80
APPENDIX		
SPECIFICATIONS COVERING CAST TITANIUM AND TITANIUM ALLOYS		. 81
REFERENCES		. 102

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	Commercial Consumable-Electrode, Skull-Melting Furnace	6
2.	Gating and Risering Arrangement for Centrifuge Casting	7
3.	A 3-Inch Gate Valve Cast in Unalloyed Titanium	8
4.	Developmental Bracket Cast in Ti-6Al-4V for Aircraft Engine	9
5.	A Consumable Electrode Constructed From Foundry Returns	10
6.	Grain-Size Distribution of Granular Graphite	13
7.	Depth of Carbon Contamination in a 1/2-Inch Section of Ti-6Al-4V Alloy Castings Made in Graphite Molds	. 15
8.	Tensile Properties of Ti-6Al-4V Alloy Castings at Elevated Temperatures	. 20
9.	Tensile Properties of Unalloyed Titanium Castings at Elevated Temperatures	. 20
10.	Effect of Removal of the Carbon-Contaminated Skin on the Fracture Strength of Cast Ti-6Al-4V Alloy	. 21
11.	Hardness and Tensile Properties Versus Oxygen Equivalent	. 25
12.	Per Cent Elongation Versus Temperature for Ti-O Alloys	. 25
13.	Extraction of Titanium (Chlorination, Distillation, Sodium-Reduction Process)	. 27
14.	Oxygen Content of Titanium Sponge as a Function of Specific Surface	. 32

LIST OF ILLUSTRATIONS (Continued)

Figure	Title	Page
15.	Hydrogen Content of Titanium Sponge as a Function of Specific Surface	32
16.	Flow Sheet for Comminution of Titanium According to U. S. Patent 2,892,697	33
17.	Isotherms at Four Different Temperatures for the Hydrogen-Titanium System	34
18.	Density Distribution in a Cold-Pressed Metal-Powder Compact	36
19.	Examples of Design Factors That May Need to be Considered in Powder-Metallurgy Parts	38
20.	Powder-Fill Examples	39
21.	Relation Between Four Pressed Shapes and Their Antecedent Die-Fill Configurations	41
22.	Pressing Stages in the Compaction to Simple Shapes .	41
23.	Relation Between Density of Green Compacts and Compacting Pressure	42
24.	Effect of Pressing and Sintering Variables on Densities of Type A Titanium Powder	43
25.	Effect of Compacting Pressure and Sintering Atmosphere on Density and Tensile Strength of Type B Titanium Powder	45
26.	Effect of Particle Size on the Sintered Density and Arc-Melted Hardness of Titanium	48
27.	Effect of Prolonged Sintering Time on the Sintered Density of Titanium	48

LIST OF ILLUSTRATIONS (Continued)

Figure	Title	Page
28.	Metal-to-Metal Oxide Equilibria in Hydrogen Atmospheres	49
29.	Clevite (Brush) Press Used in the Hot Pressing of Titanium Powders	50
30.	Strength Properties of Titanium Alloys	59
31.	Comparison of the Mechanical Properties of Ti-4Al-4Mn Alloy in the Sintered, Sintered and Forged, and Cast and Wrought Conditions	59
32.	Stress Versus Log Rupture Time at 800 F Resulting From Dispersions of Various Compounds in Titanium.	63
33.	Fabrication of Discontinuous Fiber Composite, Illustrating the Change in Orientation From Extrusion and Rolling	. 64
34.	Tensile Strength of Discontinuous Fiber-Reinforced Structures in Unalloyed Titanium	. 64
35.	Effect of Temperature on Tensile Strength of Fibered and Unfibered Titanium	. 65
36.	Effect of Temperature on Elastic Modulus of Fibered and Unfibered Titanium	. 65
37.	Effect of Temperature on Tensile Strengths of Dispersions in Titanium	. 66
38.	Effect of Temperature on Tensile Strength of Fibered and Unfibered 90 Per Cent Ti-6Al-4V Alloy	. 66
39.	Processing Steps Required to Make Parts by Powder-Metallurgy Compared With Wrought Products	. 67

LIST OF ILLUSTRATIONS (Continued)

Figure	Title	Page
40.	Examples of Titanium Parts Made by Powder-Metallurgy Processing	69
41.	Effect of Average Particle Diameter of Atomized Aluminum on Explosibility Index	71
42.	Schematic of a Typical Nontransferred Arc Type of Plasma-Arc Torch Employed for Metal-Spraying Applications	74

LIST OF TABLES

Table	Title	Page
I.	Effects of Mold Materials on Properties of Ti-6Al-4V Alloy	15
II.	Property Specifications for Titanium Castings	18
III.	Typical Mechanical Properties for Titanium Castings.	18
IV.	Typical Tensile Properties for Ti-5Al-2 $\frac{1}{2}$ Sn Castings With Very Low Interstitial Elements	19
v.	Tensile Properties of Unalloyed Titanium and Ti-2Cu Alloy	22
VI.	Standard Free Energies of Formation	24
VII.	Solubilities of Impurities Found to be Most Significant in Their Effect on Mechanical Properties of Titanium	24
VIII.	Production of Titanium- (and Zirconium) Metal Powder	29
IX.	Purity Requirement for the Purchase of Magnesium-Reduced Titanium Sponge - U. S. Government Specification	30
x.	Purity Requirements for the Purchase of Sodium-Reduced Titanium Sponge - U. S. Government Specification	30
XI.	Impurities Corresponding to Three Titanium Materials	31
XII.	Specific Surface Versus Average Particle Size for Titanium Sponge Made by Various Procedures	31
XIII.	Typical Analyses of Relatively Coarse Titanium Powder	. 32
XIV.	Analyses of Powder-Metallurgy Parts	. 34

LIST OF TABLES (Continued)

Table	Title		Page
XV.	Properties of Sintered Compacts Made From Titanium-Hydride Powders Having Different Particle-Size Characteristics		35
XVI.	Effect of Pressing Pressure Upon Density of Parts Pressed From Pure Titanium		42
XVII.	Shrinkage and Densification of Vacuum-Sintered (10-5 mm Hg) Compacts Pressed at 40 tsi Using -150 +300-Mesh Hydrided Titanium		45
XVIII.	Mechanical and Physical Properties of Pressed and Sintered Unalloyed Titanium		46
XIX.	Analyses and Properties Corresponding to Hot-Pressed and Press-Formed Titanium		51
XX.	Typical Data on the Cold Isostatic Compaction of Titanium		53
XXI.	Density of Titanium Strip		54
XXII.	Hardness of Titanium Strip		54
XXIII.	Tensile Strength of Titanium Strip		55
XXIV.	Explosive Compaction of Titanium and Other Metal Powders		55
XXV.	Summary of Pressing and Sintering Schedules Used in the Production of a Number of Alloys .		57
XXVI.	Mechanical and Physical Properties of Pressed and Sintered 2 Per Cent Aluminum Alloy		58
XXVII.	Mechanical and Physical Properties of Pressed and Sintered 6Al-4V Alloy		58

LIST OF TABLES (Continued)

Table	Title	Page
XXVIII.	Room-Temperature Mechanical Properties of Sintered Ti-4Al-4Mn Alloy in Various Heat-Treated Conditions	60
XXIX.	Mechanical Properties of Sintered and Forged Ti-4Al-4Mn Alloy Creep Tested at 200 and 400 C	61
xxx.	Material Utilization Factors for Hot-Pressed J73 Bearing Housings	68
XXXI.	Cost Reduction on Several J73 Bearing Housings	68
XXXII.	Ignition Temperatures and Explosibility of Metal Powders	70
XXXIII.	Spray Materials and Substrates for Potential Plasma-Spray Applications	73

TECHNICAL MEMORANDUM X-53437

THE MAKING OF TITANIUM AND TITANIUM-ALLOY SHAPES
BY CASTING, POWDER METALLURGY, AND OTHER PROCESSES

SUMMARY

CASTINGS

Because of its high reactivity with air, titanium is melted and cast in a vacuum. Furnaces are available for melting up to 600 pounds of titanium. The furnaces employ consumable electrodes and have a water-cooled copper crucible. A skull of solid titanium forms against the crucible and thereby prevents contamination of the molten titanium. Power input is controlled so that a suitable skull thickness is maintained.

Molds for casting titanium may be made of mild steel, copper, solid graphite or a rammed graphite mixture. Metal molds produce castings that are essentially free from surface contamination, but they have a strong chilling effect and the castings are apt to have surface laps. Most castings are made in rammed graphite molds. The surfaces of the castings are contaminated with carbon to depths of 15 to 30 mils. This contamination does no harm to corrosion resistance, but does reduce resistance to fatigue. It is common practice, therefore, to remove about 15 mils from the surface by pickling. Surface finish of castings made in rammed molds is about 120 to 300 microinches, rms. This is similar to the finish on sand castings of the more common metals.

Although titanium castings became available late in the 1950's, production increased slowly until about 1963, mainly because of their high cost. Since then lower sponge costs have permitted reductions in the price of castings. The lower prices, in turn, have stimulated increased consumption. Materials being cast include unalloyed titanium and the Ti-6Al-4V and Ti-5Al-2½Sn alloys. Titanium and titanium-alloy castings of good quality can be purchased from at least two sources, Oremet and TMCA.

POWDER-METALLURGY PRODUCTS

Powder metallurgy has been shown to be a practical method for making titanium parts. Currently, powder-metallurgy parts can be purchased from at least one supplier. Titanium sponge, made either by sodium or magnesium reduction of titanium tetrachloride, can serve as the starting material for making titanium powder. Sodium-reduced sponge is more friable and, therefore, may be the preferred material. By wet attrition milling in ice water it is possible to convert the sponge into powder of satisfactory purity. The sponge may also be embrittled by hydriding to make it more easily crushed. Titanium-powder size of -100 + 300 mesh is well suited for pressing into parts.

Titanium powder may be cold pressed at pressures generally between 30 and 50 tsi, then sintered in vacuum or a high-purity-argon atmosphere. Vacuum of about 10^{-4} mm of mercury seems to be the preferred atmosphere. The sintering temperature may be 2000 to 2350 F, depending upon specific circumstances. Vacuum hot pressing in machined graphite molds is a second procedure particularly suited to making relatively small numbers of a given part. Hot pressing is usually carried out at about 1560 to 1650 F. Both procedures can result in parts of high density and having mechanical and corrosion properties similar to those of forged material. In addition to unalloyed titanium, a variety of titanium-manganese, titaniumaluminum, and titanium-aluminum-vanadium alloys have been made successfully by powder metallurgy. Although elemental powders have been used in the past, prealloyed powders, if available, probably should permit shorter sintering periods and/or lower sintering temperatures.

Consolidation of titanium powders by roll compacting is readily accomplished. However, the requirement for high-purity argon- or vacuum-sintering atmospheres creates a serious block to the continuous production of strip by this method. Vacuum or argon sintering of the green strip in coil form would seem to be feasible.

Other methods of consolidation can be used with titanium powder just as they can with the more common metal powders. These include cold and hot isostatic compaction, high-velocity compaction, and loose-powder sintering. However, these methods have not been used to any extent with titanium powders.

Currently, there is interest in improving the strength properties of titanium through incorporation of inert materials, both in the form of dispersed particles and by use of fibers. Thorium oxide is an example of a dispersed particle. Strengthening with molybdenum and tungsten fibers is under investigation.

SPRAYED BODIES

Spraying as a means of applying titanium coatings to other materials or for making free-standing shapes has received very little attention. Plasma spraying of titanium appears to be feasible, if there were any economic or technological justification for doing so. Formation of metal-to-ceramic seals appears to be a potential application. Also, there may be justification for use of spraying in the future to restore worn areas on any costly titanium parts.

ELECTROFORMS

Titanium has been electrodeposited on steel mandrels from molten salts at 1400 to 1740 F. Hollow cylinders and vessels were formed in this manner. However, with other cheaper methods available for fabricating titanium there is little incentive for use of electroforming.

CHEMICAL VAPOR DEPOSITION

Dense microcrystalline deposits of titanium can be produced by thermal decomposition of titanium tetrabromide at temperatures of 1832 to 2552 F. By depositing onto a suitable disposable mandrel, it would be possible to produce titanium shapes. There is no record of chemical vapor deposition being used for this purpose.

INTRODUCTION

Most of the titanium and titanium alloys presently used are wrought materials arrived at by melting sponge, casting into ingots, rolling into mill shapes, then forging and/or machining into the desired final shapes. This is an involved process requiring a number of costly operations which, for many parts might well be circumvented through use of other alternative procedures. The two most promising alternatives, casting of shapes and using powdermetallurgy techniques, are not new. Both procedures were used to a limited extent in the early development of titanium. They were bypassed for the most part because the wrought material seemed to offer a better chance to ensure the high quality of parts required for the aircraft industry. Gradual improvements in technology in both fields make reconsideration of these methods as a cost-saving measure of considerable interest. Also, in some instances it is possible

to attain specific properties by means of powder metallurgy that cannot be achieved by other methods, for example, controlled densities less than theoretical and formation of composite materials having unique strength properties.

It is the purpose of this report to present the state of the art in making titanium parts by methods other than machining from wrought materials. The methods included are casting, powder metallurgy, electroforming, metal spraying, and chemical vapor deposition. The sources of information include the open literature, unpublished reports on Government contracts, and personal contacts with leading authorities in the respective fields.

SHAPING BY CASTING

HISTORICAL BACKGROUND

The development of methods to produce titanium castings started in the early 1950's. Castings became commercially available in the late 1950's. Subsequent growth of the industry was slow chiefly because the high cost of castings obstructed a brisk demand for them. Low demand hindered the development of production improvements and attainment of production experience. Production experience was gained concurrently as the price of the melting stock (titanium sponge) dropped from the original Government-supported price of \$5/lb to the current price of \$1.32/lb. By 1962, the titanium-casting market had grown to about 10,000 annual pounds; the average price was \$20/lb. A marked continuing upward demand trend established in the latter part of 1963 resulted in doubling of the sales (Ref. 1), and the selling price was reduced by about 25 per cent (Ref. 2). A typical 50-pound casting was then priced as low as \$16/lb and larger castings were priced as low as \$9/lb. These are also the current prices and are comparable with those for Hastelloy C castings of equal size when the weight difference is taken into consideration.

By far, the bulk of the present market is supplied by the Oregon Metallurgical Corporation (Oremet) at Albany, Oregon. Titanium Metals Corporation of America (TMCA) at Henderson, Nevada, uses a proprietary process to supply castings that are relatively small in size and simple in shape.

MELTING METHOD

The chemical activity of molten titanium is so great that it cannot be contained in any known crucible material without becoming contaminated. The only way that the molten metal can be held and handled is in a cooled crucible against which molten titanium solidifies to form a solid lining or "skull", and thus protects the remaining molten titanium from reacting with the crucible proper. Hence the term skull-melting furnace.

In skull melting, a consumable electrode of titanium or titanium alloy is melted under vacuum in a water-cooled copper crucible. At a high current density, the electrode melts down rapidly to form a superheated melt, which is then poured immediately within the vacuum chamber. Drastic water cooling of the copper crucible maintains the thin titanium skull as a noncontaminating lining surrounding the melt at all times. After completion of the pour, about onequarter of the melt remains as the skull lining.

The schematic diagram in Figure 1 shows the essential details of a commercial skull-melting furnace used by Oremet, which is based on the original development by the Albany, Oregon, station of the Bureau of Mines. This furnace has a maximum melt capacity of 600 pounds of titanium. The crucible tilts to pour the melt into a funnel (not shown), which leads the stream into the mold cavity. For maximum productivity per melt cycle, multiple castings are poured whenever possible to utilize the full capacity of the crucible. Castings can be made either in static molds or in molds centrifuged about a vertical axis. Centrifuge casting is preferred because it minimizes problems with gas porosity. A typical gating arrangement for centrifuge casting is shown in Figure 2. Examples of castings are presented in Figures 3 and 4.

Figure 5 shows a consumable electrode consisting entirely of cleaned foundry returns joined together by the Heliarc welding process. Repeated recycling of foundry returns gradually builds up the interstitial content (carbon, oxygen, and nitrogen), which strengthens the castings but decreases their ductility. To restrict this buildup, the normal practice is to use about 75 per cent foundry returns in constructing the electrode (Ref. 5). The balance of the electrode consists of material that is low in interstitial content, i.e., product vacuum arc melted from a compacted-sponge electrode (alloyed or unalloyed) in a water-cooled copper ingot mold. Also up to 25 per cent of the anticipated melt may consist of foundry returns or clean

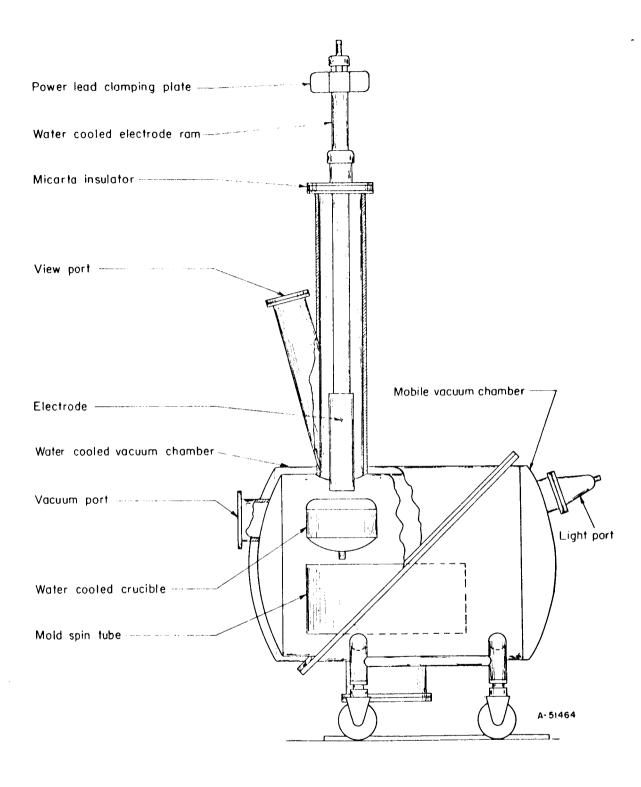


FIGURE 1. COMMERCIAL CONSUMABLE-ELECTRODE, SKULL-MELTING FURNACE (REF. 3)



FIGURE 2. GATING AND RISERING ARRANGEMENT FOR CENTRIFUGE CASTING (REF. 4)

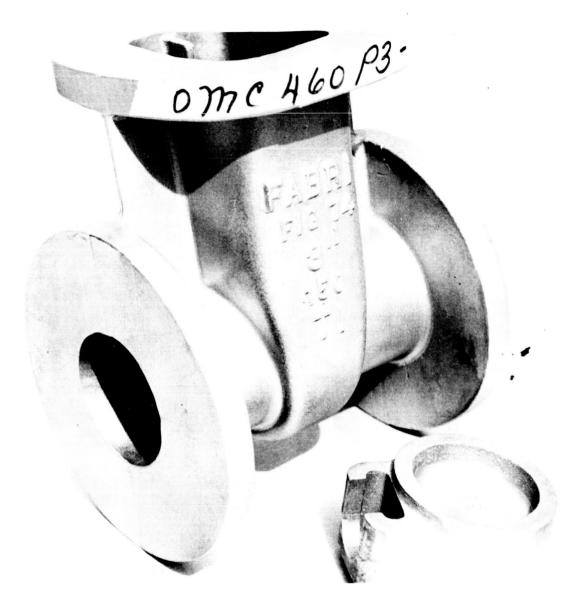


FIGURE 3. A 3-INCH GATE VALVE CAST IN UNALLOYED TITANIUM (REF. 4)

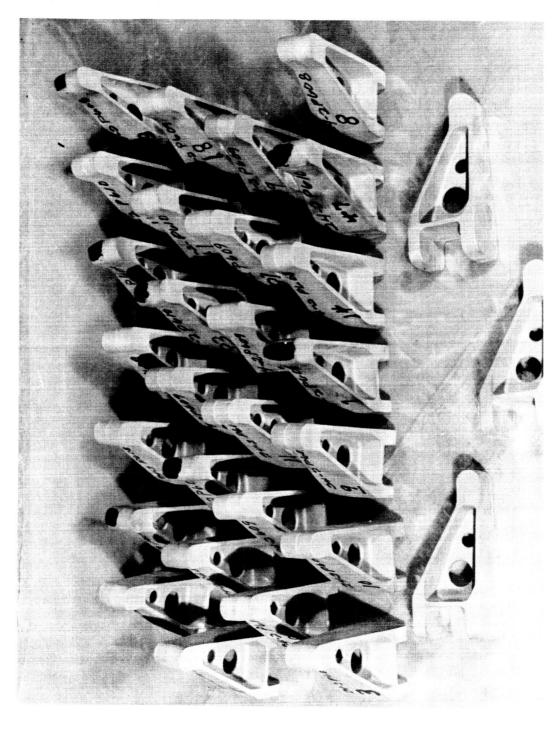


FIGURE 4. DEVELOPMENTAL BRACKET CAST IN Ti-6Al-4V FOR AIRCRAFT ENGINE (REF. 4)

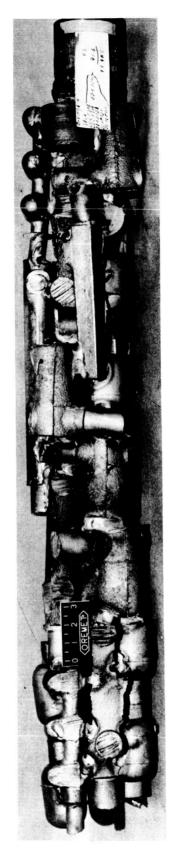


FIGURE 5. A CONSUMABLE ELECTRODE CONSTRUCTED FROM FOUNDRY RETURNS (REF. 4)

turnings placed as an additional starting pad in the bottom of the crucible. This practice saves the expense of welding the pieces to the electrode.

A typical melting procedure is as follows (Ref. 4). The electrode and molds are assembled in the furnace. The furnace is sealed and pumped down to less than 50 microns' pressure. With the electrode at negative potential with respect to the crucible, an arc is struck at about 5000 amperes and 30 volts. Within about 4 minutes, this is adjusted to 12,000 amperes and 40 volts for a 9-inch-diameter crucible or 14,000 amperes, 42 volts for a 12-inch crucible and 23,000 amperes and 38 volts for a 16- or 20-inch crucible. The two largest crucibles (Ref. 5) in common use now have an electrode measuring 12 inches in diameter. The electrode is lowered as its tip melts off. The melting rate is about 20 pounds per minute.

When the desired amount of metal has been melted, the arc is extinguished and, within 4 to 7 seconds, the electrode stub is retracted and the melt is poured. The pouring must be rapid or an excessive amount of the melt is retained in the crucible as an unnecessarily thick skull. Such an occurrence can result in insufficient metal for filling the mold.

A large graphite funnel is used to collect the melt during the rapid pour and to direct it into the sprue of the mold. When the pour is completed, the furnace chamber is backfilled with argon. After a lapse of about an hour, the furnace shell is opened and the mold is removed. A complete cycle time for melting and casting averages about 3 hours (Ref. 6).

MOLDING MATERIALS

Mold materials that are sufficiently inert for casting titanium are copper or steel, solid graphite, and a rammable graphite mixture (Refs. 3,7) that requires firing at a high temperature. Molds machined from copper, steel, or solid graphite (Grade CS) are suitable only for simple shapes that do not restrict the contraction of the casting during solidification. If the restriction to solidification contraction is severe enough to cause hot tears in the casting, then a rammed graphite mold or core must be used.

Impel Process. Mild steel is used as a permanent mold in the TMCA Impel casting process, which is a form of die casting (Ref. 8). Size limitations on Impel castings are 5 by 10 by 24 inches.

Maximum section thickness is 1/2 inch without encountering porosity or shrinkage voids. The minimum section that can be run is about 1/16 inch. A minimum draft of about 1/64 inch per inch is desired for easy injection of the casting out of the mold. Cores as long as 12 inches can be pulled. A typical finish is better than 100 microinches, rms. There is insufficient experience to specify dimensional tolerances.

Impel castings are essentially free of contamination because of the lack of metal-mold reaction. The ASTM specification B 367-61T is applicable to Impel castings (see the Appendix).

As an example of die life in the TMCA process, 100 shots can be made of a 12-pound pump impeller. Nine castings of an impeller, which is 9 inches in diameter and has five blades, are required to write off the cost of the die and make the price per casting competitive with the price (\$500) for an impeller fabricated by welding. It has been estimated that an order for 25 would bring the price per casting to half that of an impeller fabricated by welding.

Oremet Practice. In the Oremet practice, machined graphite molds have a life of between 12 and 20 castings and are best suited for casting simple shapes or very large sections. However, molds machined from graphite, copper, or steel have such a strong chilling effect that castings are apt to have surface laps. The majority of castings are now made in rammed graphite molds because these molds are less apt to produce surface laps or hot tears and because they are generally less expensive than machined molds.

Rammed graphite molds are expendable in that they are used only once. However, the molding material is reclaimable. Block graphite in tube form is used for sprues and runners.

In some casting designs where a core is to be used, but is not surrounded by massive amounts of metal, a graphite shell core is desirable (Ref. 3). It is desirable because it can be cleaned out of the casting much easier than a rammed graphite core. Also, as discussed later, the shell core increases the length of a section that can be fed by a riser.

The rammable graphite mixture currently in use is a variation of the original mixture developed by Field (Ref. 9). The formula is as follows (Refs. 3,4):

Material	Weight Per Cent
BB5 granular graphite	70
Laundry starch	5
Foundry pitch	10
C-3 carbonaceous cement	8
Water	7

Figure 6 gives the grain-size distribution of the graphite powder. The carbonaceous cement is a proprietary product produced by the National Carbon Company.

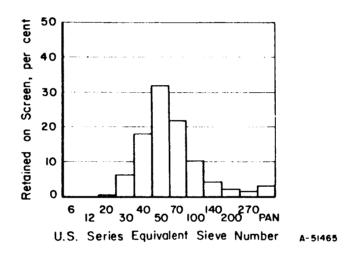


FIGURE 6. GRAIN-SIZE DISTRIBUTION OF GRANULAR GRAPHITE (REF. 4)

Preparation of the ramming mix is as follows (Refs. 3,4). The graphite and starch are mulled for 2 minutes; then the pitch is added and mulled for 2 minutes. Water and the carbonaceous cement are added and mulled for 4 minutes. Dense green molds are produced with conventional patterns by using a pneumatic bench rammer (Ref. 4). A vibrating draw machine minimizes dimensional variations in the mold during stripping of the pattern. Green molds normally have an AFS hardness of 80, compressive strength of 7 psi, and an AFS permeability of 190. After firing the strength is 70 psi.

The green molds are placed on graphite plates for handling through the firing cycle (Ref. 4). First the green molds are air dried for a minimum of 8 hours for slow removal of the moisture. Most of the remaining moisture is removed by baking for a minimum of 16 hours at 250 F. Then they are packed in graphite powder in heat-resistant boxes and placed in an electrically heated furnace at 1200 F, after which the furnace temperature is raised to 1600 F. The molds are held at this temperature for 8 to 24 hours, depending upon the mass of the molds (Ref. 5). After firing they are removed and cooled in a vacuum chamber (Ref. 4). The molds are stored in an oven at 250 F to avoid pickup of moisture. Molds are assembled and sealed in the skull furnace within a period of 2 hours after removal from the storage oven to assure a low pickup of moisture. Assembly of the molds is accomplished with steel clamps and bolts. The cycle time for mold preparation is 5 to 6 days (Ref. 5).

The mixture for shell cores consists of 80 per cent BB5 granular graphite, 8 per cent pitch, and 12 per cent phenol-formaldehyde (Ref. 3). These materials are mulled for 5 minutes. With an air pressure of 20 to 25 psig, the mix is forced into the core box and densified. The core box, constructed of aluminum or block graphite, is maintained at 250 F. An application of silicone grease plus a spray with a silicone-water emulsion serves as a parting agent before investing each shell. The shell forms in an 8-second dwell time. Then the shell is cured in the core box for a minimum of 1 minute before it is stripped. It is subjected to the same firing cycle as the rammed molds except that the initial low-temperature portion of the cycle is omitted.

Graphite molds as a class contaminate the skin of castings with carbon to a maximum depth of about 30 mils and an average depth of 15 to 20 mils as shown in Figure 7. This does no serious damage to the corrosion resistance of the casting but, as shown later, chemical removal of 15 mils of the surface markedly improves the fatigue-endurance strength. The commonly used solution (Ref. 3) consists of:

2 parts nitric acid
3 parts hydrochloric acid
Hydrofluoric acid
Acetic acid or
oxalic acid
Disodium phosphate
Wetting agent such as "Ultrawet
K", Atlantic Refining Company

15 to 25 oz/gal
5 to 9 oz/gal
3 to 8 oz/gal
3 to 4 oz/gal
0.3 to 0.4 oz/gal
0.1 to 0.2 oz/gal
To adjust surface tension
to 30 to 40 dynes/cm

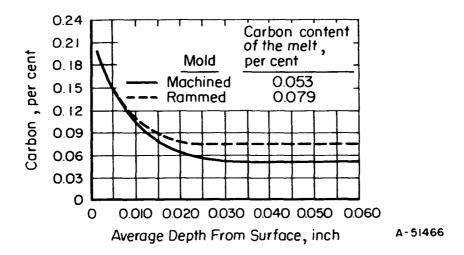


FIGURE 7. DEPTH OF CARBON CONTAMINATION IN A 1/2-INCH SECTION OF Ti-6Al-4V ALLOY CASTINGS MADE IN GRAPHITE MOLDS (REF. 10)

The life of the pickling solution is limited to the removal of 20 ounces of titanium per gallon. Rate of removal of metal ranges from 0.3 mil per minute at a solution temperature of 90 F to 1.5 mils per minute at 130 F. Castings must be cleaned of mold particles and surface oxidation before pickling and washed in water after pickling. Blasting with sand or chilled iron grit is an effective cleaning method. Metallic grit blasting without light pickling leaves a coating of iron dust on the casting that later shows up as a rusty surface. Garnet grit is used on production castings to eliminate this problem (Ref. 5).

CASTING CHARACTERISTICS

Effect of Mold Materials on Properties. Mold materials have little effect on the mechanical properties of titanium as illustrated by the data in Table I for Ti-6Al-4V alloy castings (Ref. 3).

TABLE I. EFFECTS OF MOLD MATERIALS ON PROPERTIES OF Ti-6A1-4V ALLOY

Mold Material	Ultimate Tensile Strength, ksi	Yield Strength (0.2 Per Cent Offset), ksi	Elongation, per cent	Reduction of Area, per cent	Notch Tensile Strength, ksi ^(a)
Machined graphite	135	116	7. ს	1 3. 0	205
Rammed graphite	1 35	115	7. G	13.0	194
Shell graphite	137.6	120	5. 5	10.1	198
Copper	137.5	118	7.1	8.3	205

⁽a) $K_t \approx 3.37$.

Soundness of Castings. The feeding distance is the length of section that can be made sound as a result of a riser supplying liquid metal for the solidification shrinkage occurring in the section. For an untapered plate cast in an unheated machined graphite mold, the feeding distance is equal to the thickness of the plate (Ref. 3). Beyond this distance, centerline shrinkage will occur. Casting in a heated mold does not improve the feeding distance. However, a heated machined graphite mold does decrease the gas porosity in the casting, presumably because of lower moisture content in the mold at the time of pouring. A taper of at least 4 degrees must be present in a machined graphite mold before any feeding improvement takes place. In a rammed mold for a plate about 1/2 inch thick, for example, a taper of 4 degrees doubles the feeding distance. Increasing the amount of taper progressively improves the feeding distance in both types of mold. The effectiveness of a taper decreases as the section thickness increases. A parabolic type of taper that is reduced to zero at the feeding source is much more effective than a straight taper. Because of its lower heat capacity, a shell graphite core has a feeding distance that is 1-1/2 times greater than a rammed core.

It is reported that the feeding distance is essentially the same whether the mold is used for static casting or centrifuge casting (Ref. 3). For minimum turbulence in the mold cavity during centrifuge casting, the stream should flow to the part of the mold farthest away from the vertical axis and then enter into the trailing side of the mold. Centrifuge casting at high speed (up to 600 rpm, depending upon the weight of the casting and the radius of rotation) minimizes problems with gas porosity.

Gas porosity is not a serious problem in centrifuge castings. However, porosity resulting from shrinkage is a problem. A shrinkage void is apt to be present in long thin webs that cannot be fed adequately and in heavy isolated sections such as bosses and lugs, which are the last areas to solidify. The first condition is corrected by using a graphite shell core for that portion of the mold and/or sufficient taper for adequate feeding of the section. The second condition is corrected by padding and risering. The diameter of the junction of the riser should be at least two times the thickness of the section being fed. The volume of the riser is about the same as would be used for steel castings.

Size Limitations and Casting Yield. Size limitations for static and centrifuge castings are those that fit within the space

limitations of the casting chamber, i.e., 54 inches in diameter and 30 inches in height (Ref. 5). Maximum poured weight is about 400 pounds. The minimum section thickness that can be run is 3/32 inch. Horizontal centrifugal tube castings may be produced to 6 feet in length and 24 inches in diameter.

Casting yield (trimmed casting weight/weight of metal poured) depends upon the size, shape, and number of castings made in one pour. Making multiple castings per pour within the space limitations of Oremet's present skull-melting furnace provides an average yield of 25 to 40 per cent. This compares favorably with the yield that foundries obtain with steel castings (Ref. 5).

Dimensional Tolerances and Finish. For castings made in rammed graphite molds, the value for the pattern-maker's shrinkage is 3/8 inch per foot (1/8 inch for mold shrinkage and 1/4 inch for metal shrinkage) (Ref. 3). Shrinkage from firing of shell cores is about 3/16 inch per foot (Ref. 10).

General rules for dimensional tolerances on sections up to 10 inches cast in rammed molds are as follows (Ref. 3):

- (1) For sections that do not cross the parting plane of the mold, use ±0.015 inch for the first fraction of an inch and widen this by ±0.005 inch for the first inch and each additional whole inch.
- (2) For sections that cross the parting plane and are essentially perpendicular to it, use ± 0.023 inch for the first fraction of an inch and widen this by ± 0.005 inch for the first inch and each additional whole inch.

The finish on castings made in rammed molds ranges from 120 to 300 microinches, rms. This is comparable with the finish on sand castings of the more common metals. With machined graphite molds, the finish on titanium castings is about 150 microinches, rms. Shell cores give a finish that is comparable with rammed cores. When a shell core is surrounded by massive amounts of metal, those areas of the casting may have a rougher finish because of metal penetration into the core surface.

PROPERTIES OF CASTINGS

Copies of specifications covering titanium and titanium-casting alloys are presented in the Appendix. The mechanical properties in these specifications are compared in Table II.

TABLE II. PROPERTY SPECIFICATIONS FOR TITANIUM CASTINGS

Specification Design a tion	Ultimate Tensile Strength, psi	Yield Strength (0.2 Per Cent Offset), psi	Elongation, per cent	Reduction of Area, per cent	Bhn, 3000-kg load		
	Unalloye	d Titanium			·		
ASTM B367-61T, Grade C-1	65,000 min	55,000 min	12 min				
Oremet's OMC-105	65,000 to 105,000	55,000 to 95,000	12 min		235 max		
					(avg)		
	<u>Ti-6A1</u>	-4V Alloy					
A STM B367-61T, Grade C-2	130,000	120,000 min	6 min				
Oremet's OMC-164-B	137,000	120,000 min	6 min	10 min			
Ti-5A1-2½Sn Alloy							
A STM B367-61T, Grade C-3	115,000 min	105,000 min	8 min				
Oremet's OMC 166-A	115,000 min	105,000 min	1 0 min				

Typical mechanical properties of these cast metals are listed in Table III.

TABLE III. TYPICAL MECHANICAL PROPERTIES FOR TITANIUM CASTINGS (REF. 5)

	Unalloyed Ti	Ti-6Al-4V	Ti - 5A1 - 2½ Sn
Tensile Strength, psi	80,000	147,000	140,000
Yield Strength (0.2% Offset), psi	60,000	130,000	130,000
Elongation, per cent	1 3	10	11
Reduction of Area, per cent	3 5	18	22
Brinell Hardness of Base Metal, 3000-kg load	201	311	321
Modulus of Elasticity, million psi	15.5	17.0	16.0
Charpy Impact (Room Temperature), ft-lb	3	17	8
Density, 1b/in. ³	0.163	0.161	0.160

The minimum and typical values in Tables II and III can be adjusted to a certain extent by adjusting the nominal composition for special applications (Ref. 5). For example, Ti-6Al-4V castings have been produced with up to 135-ksi yield strength and 155-ksi ultimate tensile strength, yet retaining ductilities of 10 per cent elongation and 20 per cent reduction of area. Unalloyed titanium castings have been

produced with up to 75-ksi yield strength, 90-ksi ultimate tensile strength, 20 per cent elongation, and 37 per cent reduction of area. Castings of Ti-5Al-2½Sn have been produced with very low content of interstitial elements for cryogenic applications. Tensile properties of these special Ti-5Al-2½Sn castings are given in Table IV.

TABLE IV. TYPICAL TENSILE PROPERTIES FOR Ti-5A1-2½Sn CASTINGS WITH VERY LOW INTERSTITIAL ELEMENTS

	Room Temperature	-423 F
Ultimate Tensile Strength, psi	109,800	195, 900
Yield Strength, psi	99,800	160,300
Elongation, per cent	17.0	11.6

The ASTM tentative specification covers unalloyed titanium and the Ti-6Al-4V and Ti-5Al- $2\frac{1}{2}$ Sn alloys. However, Boeing's research (Ref. 3) in cooperation with Oremet led to the conclusion that unalloyed titanium and the Ti-6Al-4V alloy adequately cover the three alloys in the ASTM specification. The tensile properties of the Ti-5Al- $2\frac{1}{2}$ Sn alloy were considered to be comparable with those of Ti-6Al-4V alloy as indicated by the typical properties shown above.

Heat treatment of the alpha-beta alloy, Ti-6Al-4V, can increase the strength, but at a loss in ductility (Ref. 3). For example, a solution treatment at 1550 F followed by aging at 1100 F increased the ultimate strength by 15,000 psi and reduced the ductility to one-half of the as-cast value. Annealing at 1150 F was slightly beneficial to ductility without affecting strength and may be used when a stress-relief treatment is desired.

Figure 8 shows typical tensile properties of Ti-6Al-4V alloy castings at elevated temperatures. Useful strength is retained at temperatures up to at least 800 F. Figure 9 shows the tensile properties of unalloyed titanium at temperatures up to 800 F.

Improvement in the fatigue strength with removal of part of the carbon-contaminated skin of Ti-6Al-4V alloy castings produced in a graphite mold is presented in Figure 10. Although the depth of carbon contamination is sometimes up to 30 mils, removal of only 15 mils by pickling raised the fatigue strength from a level of 59,000 to 64,000 psi.

Research to develop a cast alloy with properties superior to those of the Ti-6Al-4V alloy has not been too encouraging (Ref. 3).

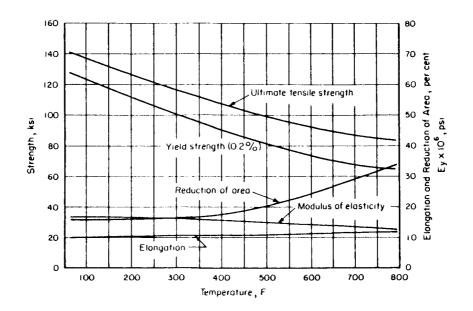


FIGURE 8. TENSILE PROPERTIES OF Ti-6A1-4V ALLOY CASTINGS AT ELEVATED TEMPERATURES (REF. 3)

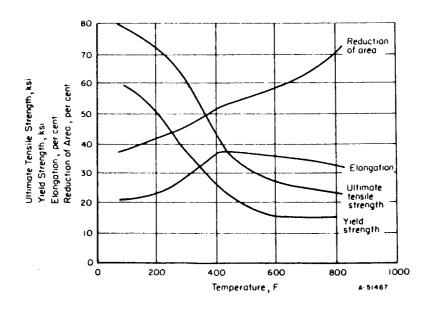


FIGURE 9. TENSILE PROPERTIES OF UNALLOYED TITANIUM CASTINGS AT ELEVATED TEMPERATURES (REF. 5)

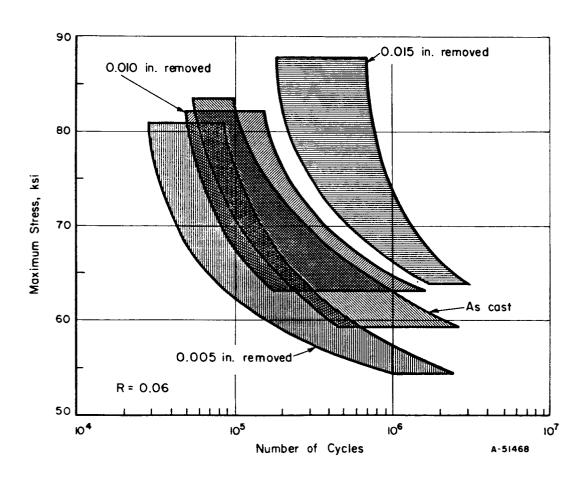


FIGURE 10. EFFECT OF REMOVAL OF THE CARBON-CONTAMINATED SKIN ON THE FATIGUE STRENGTH OF CAST Ti-6A1-4V ALLOY (REF. 3)

However, as a result of the effort that was made, Oremet has formulated tentative specifications (see Appendix) for two alloys. One of them is a Ti-4Al-8Zr-4Sn-1Fe-1Cr-1V alloy having the same minimum ductility but higher minimum yield strength and ultimate tensile strength than the Ti-6Al-4V alloy: 130,000-psi yield strength, 150,000-psi ultimate tensile strength, 6 per cent elongation, and 10 per cent reduction of area. The other new alloy is Ti-2Cu. Its minimum tensile properties are: 60,000-psi yield strength, 75,000-psi ultimate strength, 12 per cent elongation, and 20 per cent reduction of area. As shown by the data in Table V the Ti-2Cu alloy was found to have ductility superior to unalloyed titanium that was strengthened to the same level by addition of interstitial elements.

TABLE V. TENSILE PROPERTIES OF UNALLOYED TITANIUM AND Ti-2Cu ALLOY

	Tensile Properties			
	Ultimate Tensile Strength, ksi	Yield Strength (0.2 Per Cent Offset), ksi	Elongation, per cent	
Unalloyed Titanium (OMC 105) (Ref. 5)	79.3	61.1	18.5 17.0	
	82.2 77.5	62.0 61.6	18.0	
	80.7	61.1	21.5	
Ti-2Cu (Ref. 3)	79,6	62.0	25.0	
	80.0	62.0	24.0	
	79.6	61.0	25.0	

With respect to machining, all of the titanium alloys are comparable in toughness with austenitic stainless steel, except that work hardening is absent (Ref. 4). Recommended tool angles are 3-degree back rake, 3-degree side rake, 7-degree end relief, and 10-degree side relief. Cutting speed is 15 surface feet per minute with high-speed tool steels that are air cooled or flooded with conventional oil.

It may be assumed that titanium castings have the same resistance to corrosive environments as wrought titanium. In general, performance is good in oxidizing media and poor in reducing media. A number of reports cover the subject quite extensively for the wrought metal (Refs. 10,11).

FUTURE CASTING PROCESS

Production of pilot castings by a precision molding process is currently under way by an undisclosed company (Ref. 12). Commercial availability of the castings is expected in about 12 months.

The process is capable of producing complex shapes to close tolerance and very fine finish. It is believed that it will be restricted to the production of relatively small castings. In large orders the price of the castings may be as low as \$2.50/lb. From a technical and economic viewpoint this process could displace the Impel casting process. It is not likely to displace the Oremet process for the production of large castings.

SHAPING BY POWDER METALLURGY

POWDER PRODUCTION

From the standpoint of powder-metallurgy technology, the most significant characteristic of titanium metal is its reactivity toward compound-forming elements such as oxygen, nitrogen, and carbon. As a direct result, the metallurgy associated with the production of powder and with subsequent consolidation processes is strongly conditioned to allow for this reactivity. Table VI shows the reactivity of titanium toward some contaminants in comparison with that of iron, a metal commonly consolidated by powder metallurgy. The driving tendency to react, i.e., to be contaminated, is reflected in the magnitude of negative free-energy values corresponding to particular temperatures. The high negative values for the formation of titanium compounds as compared with those for iron are significant for powder production and also for subsequent fabrication operations. Also, the fact that oxygen, nitrogen, carbon, and hydrogen are appreciably soluble in titanium (Table VII) and that powders in general have high surface/volume ratios contribute to contamination by these elements.

Nitrogen, oxygen, and carbon in that order are the most significant embrittling agents for titanium. Figure 11 illustrates the strengthening and embrittling effects of these three elements in terms of an oxygen equivalent. The embrittling tendency is shown by the rapid hardness and tensile-strength increases and the drop in the reduction of area curve with increasing oxygen equivalent. Figure 12 relates tensile elongation to testing temperatures for three levels of oxygen. Particularly at low testing temperatures oxygen content has a marked influence on ductility.

The ease of contamination of titanium powder during consolidation and the necessity for careful procedures are reasons in part for the comparatively limited production of titanium parts although powder

TABLE VI. STANDARD FREE ENERGIES OF FORMATION (REF. 13)

Compound	Т, К	$\Delta extsf{F}_{ extsf{f}}^{m{\circ}}$, cal/mol
TiO	298	-117,150
FeO	298	- 58,150
TiO	1400	-92,600
FeO	1400	-41,400
TiN	1400	49, 000
Fe ₄ N	1400	+12,500
TiC	1400	-39,600
Fe ₃ C	1400	-940

TABLE VII. SOLUBILITIES OF IMPURITIES FOUND TO BE MOST SIGNIFICANT IN THEIR EFFECT ON MECHANICAL PROPERTIES OF TITANIUM (REF. 14)

Element	Alpha Solubility, wt%	Beta Solubility, wt%
Hydrogen	0.175 (7.8 at.%) at 281 C	2.1 (50 at.%) at 640 C
Carbon	0.48 at 920 C	0.15 at 920 C
Nitrogen	7.5 at 1050 C	2 at 2020 C
Oxygen	15.5 at 1770 C	2 at 1740 C

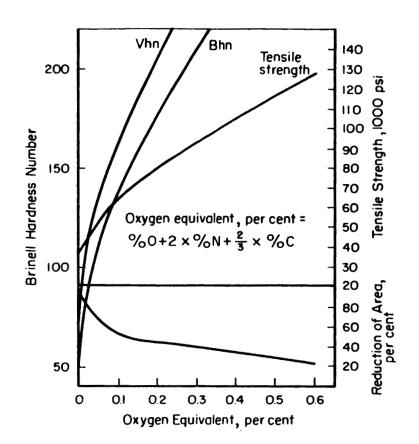


FIGURE 11. HARDNESS AND TENSILE PROPERTIES VERSUS OXYGEN EQUIVALENT (REF. 14)

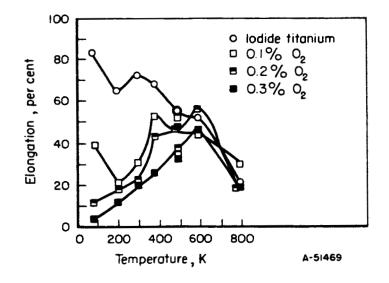


FIGURE 12. PER CENT ELONGATION VERSUS TEMPERATURE FOR Ti-O ALLOYS (REF. 14)

metallurgy was used in the pioneer production of ductile titanium (Refs. 15,16).

The production of titanium powder begins with the reduction of a compound, usually the tetrachloride to the metal in the form of a sponge. A number of approaches to the production of metal have been developed with varying degrees of success. These have been reviewed elsewhere (Refs. 17-23,25) and will not be considered in detail here. Currently, the leading processes consist of either the sodium or magnesium reduction of titanium tetrachloride. Figure 13 (Ref. 23) illustrates one procedure for making sponge by the sodium-reduction route. The process flow sheet for the magnesium reduction of the tetrachloride is similar.

For powder production the sponge is milled to finer sizes. In one procedure, the reduced mass is removed from the reduction crucible and crushed directly. As the chloride-reaction product and the titanium metal are intermingled, this material is more readily crushed than is the metal sponge after purification. The crushed product is then leached with dilute acid and dried, yielding a powder having a particle size mostly -200 mesh. The +200-mesh material can then be recycled. The product contains some magnesium and magnesium chloride (assuming the magnesium-reduction route), which cannot be completely removed by leaching, but can be eliminated by a vacuum treatment at about 1000 C (1830 F). The oxide content of the powder is usually high, owing to the leaching operation, and may be 0.3 to 0.5 per cent. Other impurities are: magnesium, about 1.00 per cent; iron, 0.05 per cent; carbon, 0.03 per cent; and nitrogen, 0.015 per cent. The powder produced by this method is ordinarily very fine, with the bulk of the metal finer than 10 microns.

An alternative procedure is that of heating the reduced sponge, containing a little magnesium, and magnesium and titanium chlorides in a vacuum. The resultant sponge metal still contains some impurities, mainly magnesium chloride. The metal is soft and cannot be comminuted readily, but can be embrittled by hydrogenation, and then milled. The particle size of the powder will vary with the degree of hydrogenation and milling. Fine powder can be produced, although the metal tends to oxidize even when precautions are taken. The oxygen content is typically ~0.20 per cent, magnesium is now about 0.30 per cent, carbon and nitrogen contents are about the same as for the leaching method, i.e., 0.03 per cent and 0.015 per cent, respectively.

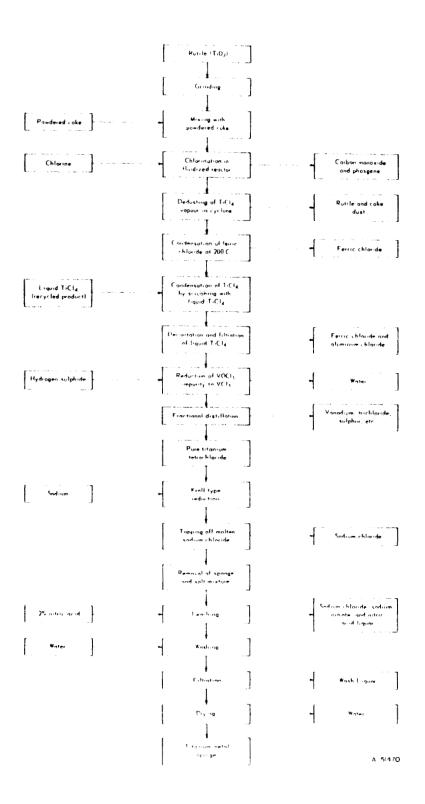


FIGURE 13. EXTRACTION OF TITANIUM (CHLORINATION, DISTILLATION, SODIUM-REDUCTION PROCESS)

Other methods of peripheral interest include electrolytic production, reduction of metallic oxide with calcium, and hydrogenation of massive metal followed by grinding. Undoubtedly, the purest titanium powder can be made by hydriding massive metal, but economic considerations restrict its use as a large-scale production method.

Table VIII from Miller (Ref. 24) summarizes some of the foregoing information. Table IX from Jamrack (Ref. 23) lists acceptable impurity levels in U. S. Government purchasing specifications for titanium sponge produced by vacuum distillation and by leaching procedures. Purity of sodium-reduced sponge can be inferred from Table X (Ref. 23) which lists impurity limits in a U. S. Government purchasing specification for sodium-reduced titanium sponge.

Table XI (Ref. 14), for purposes of comparison, notes the impurity levels corresponding to U. S. Bureau of Mines "super purity" titanium, typical iodide titanium, and a General Services Administration commercial-grade sponge.

The specific surface of titanium sponge or powder is influenced by particle size and density and is an important factor in the purity levels maintained, both during production of metal and during subsequent consolidation by a powder-metallurgy procedure. Table XII illustrates the variation in specific surface of sponge made by different procedures. Specific surface ranged from 0.1 to 0.2 m²/g for the coarsest crystalline sponge, to 5 to 6 m²/g for microcrystalline sponge. The average specific surface was 0.4 to 0.6 m²/g. Determination of oxygen and hydrogen in individual fractions showed that their contents were directly proportional to specific surface. Oxygen and hydrogen contents in relation to specific surface of one batch of titanium sponge made by sodium reduction are plotted in Figures 14 and 15. The proportional increase of contaminants illustrates the advantage of producing a coarsely crystalline material. Table XIII shows a typical analysis for -60 +100-mesh powder, which is comparatively coarse from the standpoint of customary powder-metallurgy technology.

The advantage of the coarser powder where higher purities were required was recognized earlier by Dean and associates (Ref. 16) who used powder 90 per cent of which was coarser than 200 mesh.

The production of powder from sponge is commonly done by grinding of one kind or another. A procedure for keeping contamination low during grinding is covered by U. S. Patent 2,892,697 (Ref. 26).

TABLE VIII. PRODUCTION OF TITANIUM - (AND ZIRCONIUM) METAL POWDER (REF. 24)

Metal Powder	Method of Production	Purity Level, per cent	Particle Size	Storage	Comments
Titanium (zirconium similar)	Reduction of chloride with magnesium, plus: (1) Leaching reduction product, or (2) Vacuum treatment and hydriding	O ₂ 0. 3 to 0. 5; Fe 0. 05; Mg 1. 0; C 0. 03; N ₂ 0. 015 O ₂ 0. 20; (a) Fe 0. 05; Mg 0. 30; C 0. 03; N ₂ 0. 015	0 to 5μ 50% 0 to 10 μ 100% Crushed to pass 325 mesh (Tyler): 0 to 5μ 50% 0 to 30 μ 90% 0 to 40 μ 100%	Considered safe when covered with water; zirconium is more liable to ignite than titanium	(1) Soft and porous, contains some Mg and MgCl ₂ ; (2) Rather soft and porous; contains some Mg
	Electrolytic production	$_{\rm C}$ 0.04; $_{\rm N_2}$ 0.005; $_{\rm O_2}$ (b) 0.10; Fe 0.05	As produced: 0 to 45 μ 30% 0 to 100 μ 60% 0 to 400 μ 100%		Dense particles; high purity
	Reduction of metallic oxide with calcium	O_2 0. 5 (up to 2-3); N_2 0. 05; Ca 0. 10	0 to 5 μ 70% 0 to 10 μ 95% 0 to 20 μ 100%	Generally considered safe in air owing to high oxygen content	Cheapest method, oxygen content high; very bulky
	Hydrogenation of massive metal	Similar to (2) above except Mg 0.01	Similar to (2) above	Considered safe when covered with water; zirconium is more liable to ignite than titanium	Dense and high purity

(a) Oxygen content of metal before hydriding and crushing ~0.08 per cent.

(b) Oxygen value of metallic dendrites.

TABLE IX. PURITY REQUIREMENTS FOR THE PURCHASE OF MAGNESIUM-REDUCED TITANIUM SPONGE - U. S. GOVERNMENT SPECIFICATION

After Jamrack (Ref. 23).

Impurity	In Vacuum-Distilled Titanium, per cent	In Leached Titanium, per cent
Nitrogen	0.03	0.03
Carbon	0.03	0.03
Magnesium	0.20	0.40
Chlorine	0.15	0.15
Iron	0.20	0.15
Manganese	0.20	0.20
Silicon	0.10	0.10
Hydrogen	0.005	0.03
Total of listed elements	0.70	0.80
Other metals not listed (each)	0.10	0.10
Other metals not listed (total)	0.25	0.25
Titanium (+ oxygen)	Balance	Balance

TABLE X. PURITY REQUIREMENTS FOR THE PURCHASE OF SODIUM-REDUCED TITANIUM SPONGE - U. S. GOVERNMENT SPECIFICATION

After Jamrack (Ref. 23).

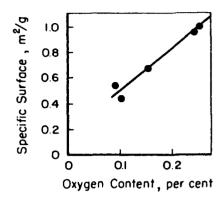
Impurity	Per Cent
Nitrogen	0.03
Carbon	0.03
Sodium	0.05
Chlorine	0.30
Iron	0.10
Manganese	0.10
Silicon	0.10
Hydrogen	0.0125
Total of listed elements	0.70
Other elements not listed (each)	0.10
Total of elements not listed	0.25
Titanium (+ oxygen)	Balance

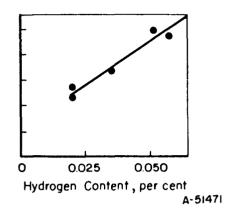
TABLE XI. IMPURITIES CORRESPONDING TO THREE TITANIUM MATERIALS (REF. 14)

		Bureau of	Mine	es - Super-	Purity	Titan	um,	per cent	_		
Fe	<0.03		Si	0.03		Al	<0.	01		С	0.01
Cr	<0.03		V	<0.02		N	<0.	001		Cl	0.09
Mg	<0.03		Mn	<0.03		Sn	<0.	03		H	0.018
Na	<0.038		Cu	<0.006		Ni	<0.	03		O	0.033
(85 Bhn predicted from oxygen-equivalent curve of Figure 11) Iodide Titanium - 99,99%: Major Impurities, per cent											
		С	4	0.0001	S	Si	0.00	15			
		O	0	to 0.002	N	4n	0.00	1			
		N	O	to 0.002	(Cu	0.00	1			
(45 Bhn expected on the basis of Figure 11)											
Sponge Titanium - Commercial Grade, per cent (To meet General Services Administration specifications)											
		Ti	min	99.3	N	lg i	nax	0.5			
		N	max	0.02		0	nax	0.15			
		C,	max	0.04	F	. I	nax	0.15			
	(B	3hn - 125	max i	f <mark>or 1</mark> 500-kg	load;	30-see	cond	dwell tin	ie)		

TABLE XII. SPECIFIC SURFACE VERSUS AVERAGE PARTICLE SIZE FOR TITANIUM SPONGE MADE BY VARIOUS PROCEDURES (REF. 27)

Sponge Particle Size, mm	Reduction of TiCl ₄ with Magnesium	TiCl_4 with	Electrolysis of TiCl ₄	
+2.5	0.33	0.57	0.61	0.35
-2.5 +1.6	0.42	0.57		0.38
-1.6 +1.0	0.51	0.65	- -	0.49
-1.0 +0.63	0.59	0.74	1.17	0.70
-0.63 +0.40	0.77	0.74	2.06	0.79
-0.40 +0.32	0.78	0.70	2.54	0.74
-0.32 +0.25	0.79	0.77	2,57	0.75
-0.25 ±0.16	0.82	0.83	2.68	0.76
-0.16 +0.10	0.90	0.88	2.79	0.74
-0.10 +0.06	0.97	0.94	3.13	0.91
-0.00 +0.05		1.00		0,99
-0.05	1, 13	1.20	4.01	1.10





SPONGE AS A FUNCTION OF SPE-CIFIC SURFACE (REF. 27)

FIGURE 14. OXYGEN CONTENT OF TITANIUM FIGURE 15. HYDROGEN CONTENT OF TITANIUM SPONGE AS A FUNCTION OF SPE-CIFIC SURFACE (REF. 27)

TABLE XIII. TYPICAL ANALYSES OF RELATIVELY COARSE TITANIUM POWDER (-60 +100 MESH) (REF. 28)

	Per	Cent
	Sample 1	Sample 2
Oxygen	0.11	0.09
Hydrogen	75 (ppm)	90 (ppm)
Nitrogen	0.07	0.02
Iron	0.02	0.06
Total light metals, as aluminum	0.07	0.085
Carbon	0.03	0.05
Heavy metals, as lead	Nil	Nil
Silicon	0.05	0.03

This patent deals with the grinding of titanium or titanium-base alloys in ice water. Figure 16 illustrates the process flow sheet covered by this patent. A suitable grinder is a rotating-disk pulverizer, lined with titanium plates. The shearing action between the rotating and the stationary disk is especially useful in comminuting sponge to powder. The feed that can be handled is not confined to the -40 +30-mesh-size range illustrated. Commonly, the sponge is milled until it passes a 100-mesh screen at which stage between 20 and 40 per cent may pass a 325-mesh screen. Open-air oxidation of the powder begins to be a problem for particles smaller than about 250 mesh.

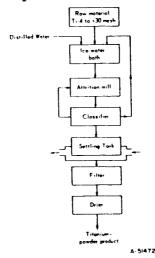


FIGURE 16. FLOW SHEET FOR COMMINUTION OF TITANIUM ACCORDING TO U. S. PATENT 2,892,697 (REF. 26)

Sodium-reduced sponge may be preferred to magnesium-reduced sponge because it is more friable and, therefore, more easily melted than the magnesium-reduced product. However, purity of sponge from both sources is ordinarily adequate. Parts made from powder generally meet the same purity specifications as titanium from arcmelted sources, as illustrated by the following analysis representative of Clevite parts (Table XIV).

Titanium may be hydrided to embrittle it for easier comminution. Absorption of hydrogen becomes rapid above about 400 C. Figure 17 from Dushman (Ref. 29) (originally from Sieverts) illustrates the uptake of hydrogen for this purpose. An example of titanium hydriding to facilitate grinding has been furnished by Rogers (Ref. 30). The operation was performed by heating titanium granules to 700 C in vacuum to condition the surface, and then allowing the granules to

TABLE XIV. ANALYSES OF POWDER-METALLURGY PARTS (REF. 31)

Per Cent

Clevite Alloy	С	N	0	Н	Fe	Al	V	Ti
CPT-2 CPT-2A CPT-64AV	0.02	0.01	0.16	0.005 0.005 0.005	0.04	2.0		Balance Balance Balance

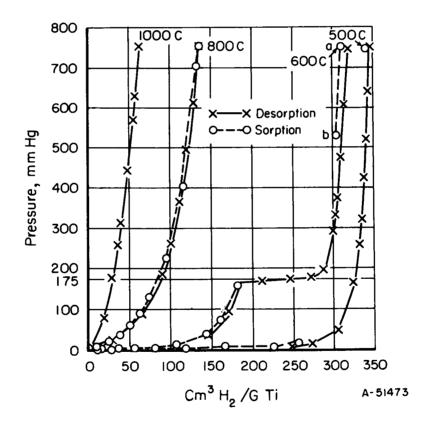


FIGURE 17. ISOTHERMS AT FOUR DIFFERENT TEMPERATURES FOR THE HYDROGEN-TITANIUM SYSTEM (REF. 29)

cool in an atmosphere of pure hydrogen. Composition of the hydride was between TiH_{1.8} and TiH_{1.9}, which would indicate complete saturation. The ball mill used to grind the embrittled titanium was fitted with a vacuum top to enable crushing to be done in an inert atmosphere. It was found that incidental contamination during hydriding and subsequent dehydriding was not very significant. Crushed 150 to 300-mesh hydride does not deteriorate on standing in air up to a month, according to Bunshah and associates (Ref. 32). Hydrogenfree powder can be produced by heating in a vacuum at 800 C (1470 F) until all of the hydrogen has been evolved.

Table XV from Robins' paper (Ref. 33) shows the increasing hardness of sintered compacts made from titanium hydrides of decreasing size fractions. The -300-mesh material would best be removed since, as indicated by the corresponding compact hardness, nitrogen and oxygen contents were excessive in this finer fraction. It is possible to remove the hydrogen from the powder by a vacuum treatment prior to pressing and sintering, but the product again becomes reactive toward contaminating gases. Therefore, it may be preferable to press the hydride powder and decompose it during the sintering process. The liberation of hydrogen during sintering accelerates the densification rate and gives a higher sintered density, possibly because of the increased mobility of the titanium atoms during decomposition of the hydride.

TABLE XV. PROPERTIES OF SINTERED COMPACTS MADE FROM TITANIUM HYDRIDE POWDERS HAVING DIFFERENT PARTICLE-SIZE CHARACTERISTICS (REF. 33)

British Standard Screen, mesh	Surface Area, sq cm/g	Average Particle Size Calculated From Surface Area, microns	Density of Compact, g/cc	Hardness of Compact, DPN
-20+30	205.0	65.04	4.22	121
-30+60	221.0	60.34	4.28	138
-60+100	273.4	48.80	4.25	150
- 100+150	335.3	39.80	4.33	189
- 150 + 200	384.4	34.70	4.31	189
- 200 + 240	496.4	26.86	4.32	184
-240+300			4.35	206
-300	1009.0	13.22	4.43	267
-100+300	471.9	28,26	4.27	181

The hydride process has been considered as a possible method of reclaiming scrap by a treatment similar to that described above for sponge. The rate of hydrogen penetration into solid metal is slow, however, and high reaction temperatures are necessary. In general, this route for powder production is too slow. The comminution of scrap before hydriding would appear to be a preferable procedure for making powder from massive scrap metal.

METHODS OF CONSOLIDATION

Conventional Cold Pressing. Although the powder metal-lurgy of titanium is unique in certain respects, primarily due to its reactive nature, it is handled, for the most part, as other metal powders. Just as a metal casting must be designed to conform to the flow and solidification processes occurring during its production, it is necessary that the designer of a powder-metallurgy part consider compacting and sintering limitations. Poor design configuration may result in parts having homogeneous section density and inadequate mechanical strength. Improper allowance for shrinkage during sintering may result in out-of-tolerance parts. It is beyond the scope of this section to discuss in detail the engineering design of powder-metallurgy parts. It is intended only to indicate the need for design considerations.

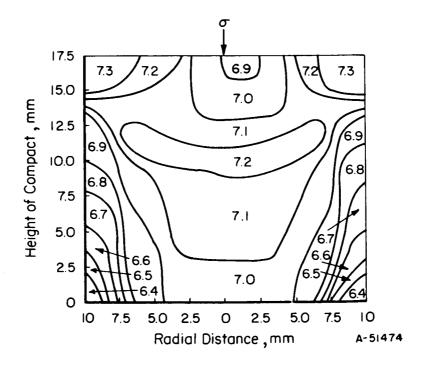


FIGURE 18. DENSITY DISTRIBUTION IN A COLD-PRESSED METAL-POWDER COMPACT (REF. 35)

Height diameter ratio: 0.87. Numbers refer to density in g/cm³.

In cold compaction of powder, uniform densification of the compact is often a problem. Figure 18 illustrates the variation in compact density obtained in even a favorably shaped die geometry. Metal powders do not behave as fluids and, therefore, compaction forces are difficult to transmit to all parts of an unfavorably disposed powder fill. For this reason long, thin-wall tubing ordinarily cannot be made by simple die compaction. Figure 19 illustrates the type of design considerations that may have to be taken into account in cold die pressing. Figure 20 shows typical examples of die-fill-section geometry for making compacted sections from loose powders. Silbereisen (Ref. 34) noted that 'the problem arising with the compacting of metal powders to complicated parts cannot be solved theoretically. It is more or less essential to study the pressing process by practical experiments. In pressing complicated pieces, false heights of die filling can create cracking and lamination". Figures 21 and 22 illustrate additional typical pressing operations. References 34,36-38 are among a number that provide design- and compaction-mechanics perspective.

The cold compactability of a titanium powder is illustrated in Figure 23 from early Bureau of Mines work (Ref. 15). Table XVI gives approximate density ranges to be expected in the as-cold-pressed and in the subsequently as-sintered conditions. The cold-pressing and sintering schedule is tailored to the part or shape being fabricated, whether it is a large billet, a rectangular sheet bar, a porous filter, or a small irregular shape in which maximum obtainable mechanical properties are expected. For titanium powder, Dean (Ref. 15) found that, with pressures above 50 psi, the increase in densification did not compensate for the disadvantages of the higher pressures involved. Low compaction pressures are desirable from die-wear considerations, but the larger attendant shrinkages during sintering are detrimental to dimensional accuracy.

In cold compaction of metal powders, about 3/4 per cent of a lubricant is normally blended with the powder prior to pressing. With most powders, such as iron, copper, nickel, etc., contamination from lubricants such as stearic acid or zinc stearate presents no serious problem. Titanium, on the other hand, may be contaminated excessively by use of such materials. However, those who have solved the lubrication problems retain their information as proprietary. Consequently, no information on lubricants is available for this report.

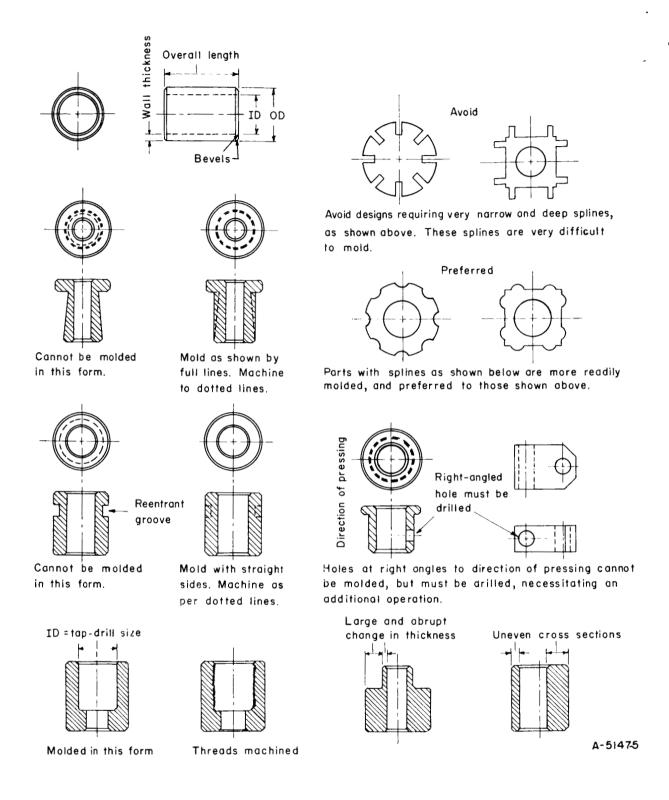


FIGURE 19. EXAMPLES OF DESIGN FACTORS THAT MAY NEED TO BE CONSIDERED IN POWDER-METALLURGY PARTS (REF. 36)

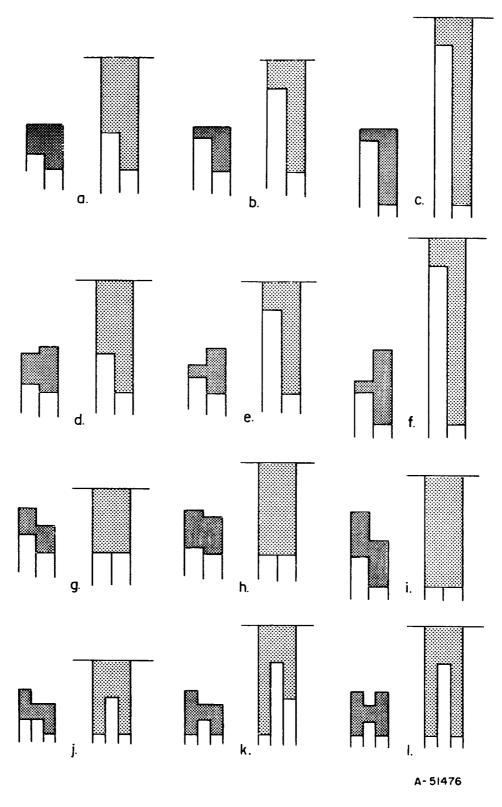


FIGURE 20. POWDER-FILL EXAMPLES (REF. 36)

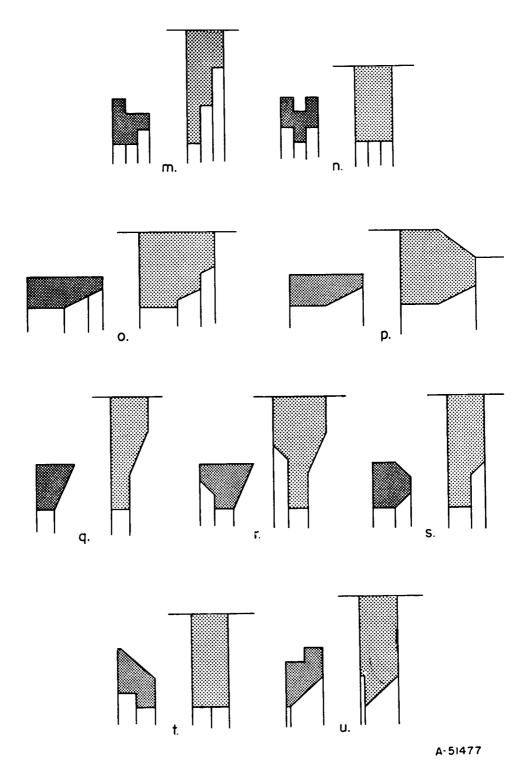


FIGURE 20. (CONTINUED)

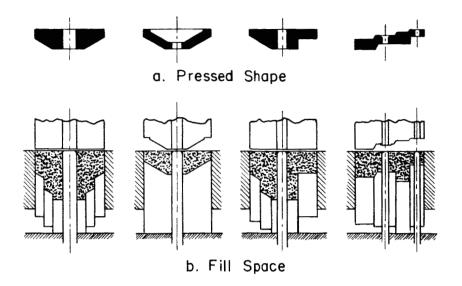


FIGURE 21. RELATION BETWEEN FOUR PRESSED SHAPES
AND THEIR ANTECEDENT DIE-FILL
CONFIGURATIONS (REF. 34)

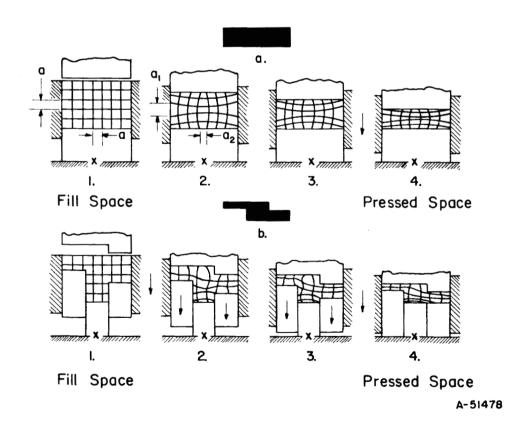


FIGURE 22. PRESSING STAGES IN THE COMPACTION TO SIMPLE SHAPES (REF. 34)

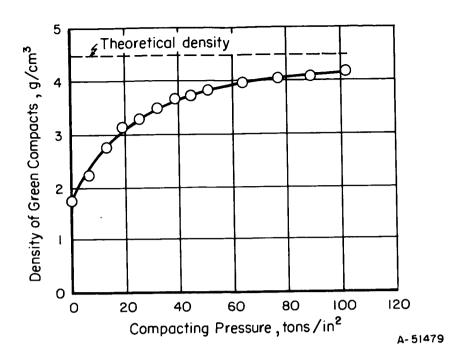


FIGURE 23. RELATION BETWEEN DENSITY OF GREEN COMPACTS AND COMPACTING PRESSURE (REF. 15)

TABLE XVI. EFFECT OF PRESSING PRESSURE UPON DENSITY OF PARTS PRESSED FROM PURE TITANIUM (REF. 28)

	Density (Per Cer	nt of Theoretical)
Tons/In. ²	After Pressing	After Sintering
30	83 to 85	87 to 90
50	90 to 93	92 to 95
60	93 to 95	95 to 97

It is expected that organic lubricants that volatilize completely without dissociation would be suitable. The principal function of the lubricant is one of die-wall lubrication, both during pressing and to assist in extraction of the pressed compact. Therefore, contamination could be kept to a minimum by using only die-wall lubrication if the production rate were low enough to permit use of this method.

Sintering Temperature and Atmosphere. The effects of variations in sintering temperature have been demonstrated using "Type A" powder of controlled particle size, i.e., 100 per cent -28 +100 mesh. Pressings 0.5 inch in diameter and 1 inch long were sintered in a vacuum furnace at a pressure not exceeding 0.05 micron of mercury for 1 hour at 1000, 1200, and 1300 C. The results (Figure 24) indicate that high densities (above 90 per cent) can be achieved by controlling sintering temperature and compacting pressure. Increasing sintering temperature had greater effect on density when low compacting pressures were used. For a compacting pressure of 100 tsi, the effect of varying the sintering temperature was reduced to an almost negligible amount.

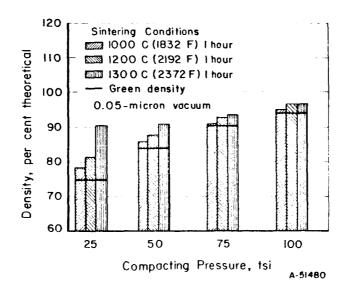


FIGURE 24. EFFECT OF PRESSING AND SINTERING VARIABLES ON DENSITIES OF TYPE A TITANIUM POWDER (REF. 39)

"Type B" powder was used in demonstrating the effect of sintering atmosphere in as-sintered strength. This powder, having the following sieve analysis, was somewhat finer than Type A.

Mesh	Per Cent
+100	0.1
-100 +200	61.3
-200 +325	28.0
-325	10.6

As shown in Figure 25, the effect of sintering atmosphere on density was negligible in comparing vacuum and argon atmospheres. Sintering in vacuum did, however, promote higher strength in titanium powder pressed at the lower compacting pressures. The effect on strength decreased when very high compacting pressures, corresponding to high cold-pressed densities, were used.

Densification and shrinkage during sintering were observed by Robins, Pitkin, and Jenkins (Ref. 40) on -150 +300-mesh hydrided titanium. The comparatively rapid sintering rate of the hydride power is evident in Table XVII.

Further data illustrating the effect of compacting pressures on as-sintered mechanical and physical properties of titanium have been presented by Weber (Ref. 41). Rather large pieces were pressed in order to minimize the effect of die-wall friction. The Type B powder used had the following sieve analysis: -100 +200 mesh, 4.5 per cent; -200 +250 mesh, 4.0 per cent; -250 +325 mesh, 37.8 per cent; -325 mesh, 53.6 per cent. The pieces were vacuum sintered for 4 hours at 2200 F and then furnace cooled. Table XVIII summarizes the data obtained. The unalloyed titanium displayed an excellent combination of strength and ductility considering that a single pressing and sintering were used. The strength was improved considerably in the pressing increment between 32 and 51 tsi. As in other work, strength and density showed signs of levelling off at a pressing pressure of 58 tsi.

Dean and associates (Ref. 15) concluded that the optimum sintering temperature for titanium-powder compacts is somewhere in the 950 to 1000 C (1740 to 1830 F) temperature range. The objection to higher temperatures lay in the embrittlement of the titanium due to leakage into the furnace, which was operated at a pressure of 1 x 10⁻⁴ mm of mercury to distill off residual magnesium and remove hydrogen. In the absence of contaminating influences there is no reason why somewhat higher sintering temperatures cannot be used. In more recent Soviet work, titanium powder was vacuum sintered at 1400 C (Ref. 42). The density achieved for any sintering temperature is partially dependent on particle size. Figure 26 from Rogers (Ref. 30)

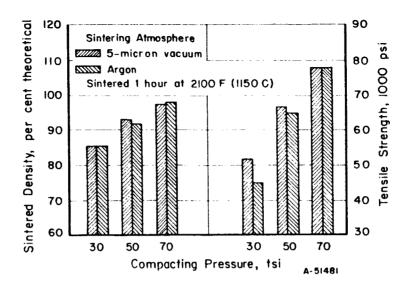


FIGURE 25. EFFECT OF COMPACTING PRESSURE AND SINTERING ATMOSPHERE ON DENSITY AND TENSILE STRENGTH OF TYPE B TITANIUM POWDER (REF. 39)

TABLE XVII. SHRINKAGE AND DENSIFICATION OF VACUUM-SINTERED (10⁻⁵ MM Hg)
COMPACTS PRESSED AT 40 TSI USING -150 +300-MESH HYDRIDED
TITANIUM (REF. 40)

Sintering Treatment			Density of Sintering		
Temperature,	Time, hr	Shrinkage, per cent	Grams per Cubic Centimeter	Per Cent of Theoretical	
1200	4	12.2	4.36	96.9	
1200	8	13.2	4.40	97.8	
1300	4	12.9	4.39	97.6	
1300	8	13.3	4.42	98.4	

TABLE X VIII. MECHANICAL AND PHYSICAL PROPERTIES OF PRESSED AND SINTERED UNALLOYED TITANIUM (REF. 41)

	Pr	Pressing Pressure			
Property	32 Tsi	_			
Tensile Strength, psi	58,000	70,000	73,000		
Yield Strength, psi (0.2% offset)	45,000	54,000	57,000		
Elongation, per cent in 1 inch	12	18	20		
Reduction of Area, per cent	15	24	25		
Hardness, R _B	71.5	85			
Brinell, 500-kg load	96.3	114			
Impact Properties (V-Notch Charpy),					
ft-lb	2.75	5.0			
Fatigue-Strength (Rotating Beam					
10,000 Cycles Per Minute) Endur-					
ance Limit, 10 ⁷ cycles			32,000		
Endurance Ratio, per cent			45		
Green Density, per cent of					
theoretical, 0.163 lb/in. ³	87.0	93.5	94.7		
Sintered Density, per cent of					
theoretical, 0.163 lb/in. ³	90.5	95.0	97.0		
Coefficient of Thermal Expansion,					
RT to 500 F Avg., microinch per					
degree F		4.11			
Electrical Resistivity, ohm-cm 10 ⁻⁶		61			
Thermal Conductivity, cal sec ⁻¹ cm ⁻²					
cm C ⁻¹		0.035			

indicates that full density was achieved by sintering 4 hours in vacuum (10-5-10-6 mm Hg) at 1250 C (2280 F). The titanium powder had an average particle size of 6 microns. On the other hand, powder averaging 28 microns in size did not exceed 96 per cent of full density under the same conditions. The penalty in contamination through the use of the finer powders is indicated by the rising TiH₂ curve corresponding to arc-melted hardness. The effect of a longer sintering time and a higher sintering temperature in densifying sodium-reduced titanium containing about 0.2 per cent NaCl and chloride-free titanium, for comparison, are shown in Figure 27. The drop in density for the contaminated titanium after several hours appeared to be associated with the internal vaporization of NaCl or possibly with the reaction

$$Ti(s) + 2NaCl(1) = TiCl_2(g) + 2Na(g)$$
.

There appeared to be no advantage in sintering for more than a few minutes at temperatures above 1250 C.

Hydrogen atmosphere is not effective in reducing oxide contamination. At 900 C hydrogen will reduce TiO₂ only to the Ti₃O₅ level (Ref. 17). Furthermore, unless hydrogen is not exceptionally dry, the titanium powder will react with the water vapor. Figure 28 indicates that titanium will be oxidized to TiO₂ during sintering in hydrogen unless the dew point is less than about -120 F. In addition, as noted earlier, a vacuum appears preferable from a strength standpoint for compacts pressed initially to lower densities. Finally, hydrogen, residual magnesium, and possibly other impurities are removed in whole or at least in part during vacuum sintering.

It has been reported, as the result of Soviet research (Ref. 43), that it is preferable to heat titanium cyclically rather than isothermally during powder sintering. The densities reached over a 16-hour period were favored by the cyclic treatment up to a temperature of 2012 F. However, similar work by Powell (Ref. 44) has shown that sintering isothermally for 5 hours yielded densities and mechanical properties that were equivalent to those obtained by cyclic sintering using Mints' schedule.

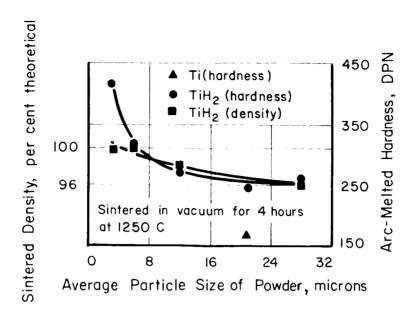


FIGURE 26. EFFECT OF PARTICLE SIZE ON THE SINTERED DENSITY AND ARC-MELTED HARDNESS OF TITANIUM (REF. 30)

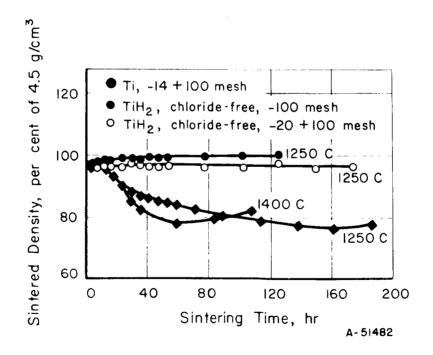


FIGURE 27. EFFECT OF PROLONGED SINTERING TIME ON THE SINTERED DENSITY OF TITANIUM (REF. 30)

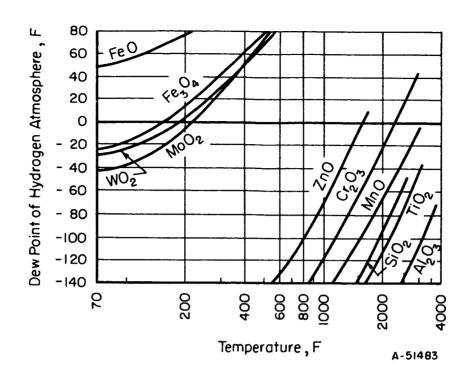


FIGURE 28. METAL-TO-METAL OXIDE EQUILIBRIA IN HYDROGEN ATMOSPHERES (REF. 45)

Hot Pressing and Press Forming. It is not unusual in powder metallurgy to employ mechanical-compaction forces either during or after sintering to obtain increased densities. The desirability of using coarse powder to minimize contamination as much as possible was noted earlier. The use of coarse powders, however, delays densification by solid-state diffusion. Two compaction procedures for coarse titanium powder largely developed by Clevite Corporation (formerly Brush Laboratories) personnel are hot pressing and press forming (Refs. 32, 42, 46-49). The first process involves vacuum (about 2 microns) hot pressing at 850 to 900 C in a graphite die. The second is better adapted to volume production and involves cold pressing in a tool steel die to a density of about 3.85 g/cm³. This is followed by vacuum sintering for about 1 hour at 1000 C (1830 F). The next operation consists of warm forming at a pressure of about 150,000 psi in a steel die preheated to 600 C (1110 F), succeeded by a second sintering operation in vacuum at 1000 C after which the piece is pressed to final shape.

Figure 29 illustrates the type of press used in the successful vacuum hot pressing of titanium powders. This does not, of course, represent the ultimate design or maximum size practical for this kind

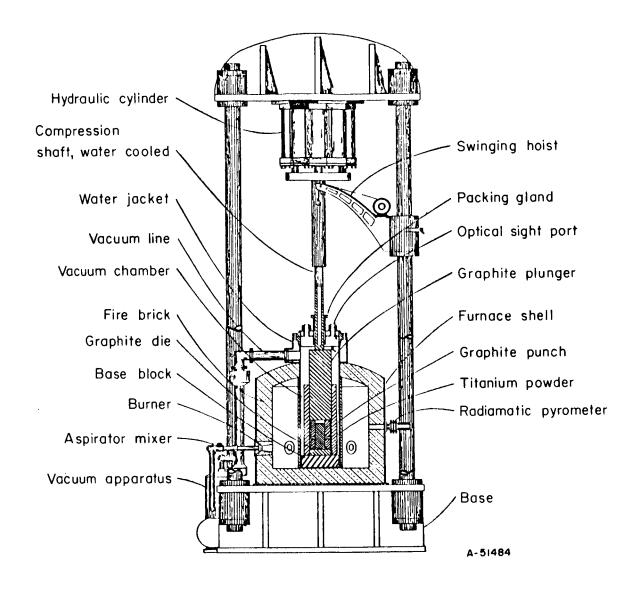


FIGURE 29. CLEVITE (BRUSH) PRESS USED IN THE HOT PRESSING OF TITANIUM POWDERS (REF. (REF. 46)

of operation. Table XIX illustrates typical properties obtained by the above two procedures.

TABLE XIX. ANALYSES AND PROPERTIES CORRESPONDING TO HOT-PRESSED AND PRESS-FORMED TITANIUM (REFS. 42, 46, 47)

	Hot Pressed	Press Formed							
Chemical Analysis, per cent									
Carbon	0.014	<0.01							
Oxygen	0.0929	0.1013							
Nitrogen	0.013	0.011							
Hydrogen	0.00189	0.000375							
Iron	0.095	0.090							
Te	nsile Properties								
0.2% Offset Yield Strength	39, 900 psi	39,300 psi							
Tensile Strength	58,400 psi	64,200 psi							
Elongation in 0.850 Inch	35.0%	42.6%							
Reduction of Area	53.3%	60.5%							
Rockwell Hardness	RA 48								
Impact Strength									
(V-Notch Charpy), ft-lb									
-318 F	32								
- 40 F	42								
79 F	36								
200 F	40								
400 F	37								

Isostatic Compaction. Isostatic compaction is applicable to the consolidation of titanium powders in the same way that it is to other metals, again with the provision that care be used in avoiding contamination. Two classes of isostatic compaction may be considered. In the first, compaction is carried out at ambient temperatures. The powder is changed into a rubber or plastic container and subjected to hydrostatic (i.e., isostatic) pressures. In the second, use of higher temperatures necessitates employment of a gas and a metallic container for the powder. This is the so-called "gas pressure bonding" process.

Typical processing equipment is described in References 50 through 52. Powell (Ref. 53) has used a pliable-mold-compaction process suitable for isostatic pressing of titanium powder. Isostatic compaction of a variety of materials has been carried out on an experimental basis at Lawrence Radiation Laboratory (Ref. 54).

Du Pont titanium sponge up to 1/8-inch maximum, Du Pont coarse sponge over 1/4 inch, and U. S. Bureau of Mines flake were compacted in stainless steel foil-lined bags. Oil was used as the pressure transmission medium. Table XX presents typical results obtained. Use of the foil liner prevented sticking and contamination by the elastomeric pressure bag.

Cold isostatic compaction is advantageous as compared with solid die pressing for the following reasons:

- (1) In general, it is possible to obtain more uniform aspressed densities in large billets or in certain shapes that would be difficult to press in solid steel dies (for example, hollow shapes).
- (2) Molds for shaping powders can be made for inexpensive materials.
- (3) Where a sealed bag of some kind is used, an inert atmosphere or a vacuum can be maintained.

Among the obvious disadvantages is that isostatic pressing is less amenable to rapid production than is high-speed die pressing. Further, specialized equipment is ordinarily required.

Titanium powder could be pressed by the hot gas-pressure sintering method. However, there appear to be no data available resulting from consolidation of titanium powder by gas-pressure sintering.

Gas-pressure sintering, in concept at least, combines the advantages of both isostatic pressing and hot pressing. It is possible through special procedures to make compacted shapes in a single press-sinter operation, which would be more difficult by other procedures. One example is the use of gas-pressure sintering to make full element structures to close dimensional tolerances and to full densities. Among the disadvantages are the problem of metal-can removal and the associated difficulty of adapting gas-pressure sintering to high-speed production.

Rolling of Powder. With the continued development of powder-metallurgy technology there has been increasing interest in continuous roll compacting to produce strip (Ref. 55). Titanium strip about 0.5 mm in thickness has been directly rolled from

TABLE XX. TYPICAL DATA ON THE COLD ISOSTATIC COMPACTION OF TITANIUM (REF. 54)

	Remarks					Good; liner removed easily		Good; liner removed with	ίτγ
			Good	Good	Good	Good; lir		Good; lir	difficulty Good
Density	Per Cent of G/CC Theoretical		89	85	90	80		88	95
	22/9		3,06	3.84	4.08	3.62		3,96	4.26
Liner	Thickness, mils		5	5	8	∞		&	σ.
Compacting	Pressure, psi		25,000	45,000	46,000	25,000		46,000	45,000
	Weight, g		2000	2570	1000	650		2750	3495
Final Compact	Size, in. Diam Length		9-1/5	13-3/4	r.	က		15-1/2	14-7/8
Final C	Size, Diam		1/2 2-1/4	c 3	2-1/16	2-3/16		20-1/2 1-7/8	2-3/16 14-7/8
	c, in. Length		13-1/2	19	∞	4		20-1/2	19
	Initial Size, in. Diam Length		2-15/16 13-1	2 - 3/4	2-15/16	2-7/8		2-1/8	2-3/4
	Material	Titanium	Fine sponge	Fine sponge	Coarse sponge	Very coarse sponge (particles >1 /4-in.	sizc)	Very coarse sponge	Flake

dehydrided powder (Ref. 56). The rolling operation itself was quite successful, but contamination could not be avoided in subsequent sintering in a high-purity argon atmosphere. Data from this effort are shown in Tables XXI, XXII, and XXIII. With adequate precautions to prevent the entrance of damaging impurities, production of strip should be feasible. Vacuum sintering of the cold-pressed strip in coil form would appear to be a possible approach. Soviet interest in powder rolling of titanium is indicated by References 57 and 58. The latter reference describes the rolling of powder, sintering, cold rolling of the strip, annealing, and cutting. A detailed treatment of the rolling mechanics is included. Sintering was of brief duration (several seconds to several minutes). Good results were obtained with a temperature of 1050 C. It is reported that strip was rolled that had a tensile strength of 70 kg/mm² (100,000 psi) and an elongation of 25 per cent.

TABLE XXI. DENSITY OF TITANIUM STRIP (REF. 56)

Sintering Time, hr	Density, g/cc	Porosity, per cent	Theoretical Density, g/cc
0	3.50	22.9	4.50
5-1/2	4.35	4.2	
8	4.34	4.4	
21	4.41	2.9	

TABLE XXII. HARDNESS OF TITANIUM STRIP (REF. 56)

Material	Hardness, DPH
Uncompacted Powder	190
Green Strip (surface, unetched)	241
Sintered for 5-1/2 Hours	561
Sintered for 8 Hours	490
Sintered for 21 Hours	426

TABLE XXIII. TENSILE STRENGTH OF TITANIUM STRIP (REF. 56)

Material	Density, g/cc	Ultimate Tensile Stress, tsi
Sintered 8 Hours	4.29	42.3
Sintered 8 Hours	4.39	41.3
Sintered 8 Hours and Cold		
Rolled 29 Per Cent		57.0
Sintered 21 Hours	4.41	16.6
Arc-Melted Commercial		
Titanium	4.5	29.47

Titanium powders can be consolidated by rolling in a sheath. A procedure was developed at the Bureau of Mines for doing this (Ref. 59). The general topic of sheath rolling has been reviewed by Williams (Ref. 60).

High-Velocity Compaction. Titanium powder, like other elemental powders, may be explosively compacted. Table XXIV compares the results of work with titanium and other powders in which canned powders were compacted with spiral-wrapped explosives. Detonation was carried out in a water bath. It was possible to form simple shapes by this procedure. Titanium was compacted in lengths up to 20 inches. The high-energy-rate compaction of a small batch of titanium powder by an explosively propelled flat-nosed projectile has been done also (Ref. 61). The small slug obtained was 97 per cent dense. The explosive compaction of metal powders in general has been reviewed by Geltman (Ref. 62).

TABLE XXIV. EXPLOSIVE COMPACTION OF TITANIUM AND OTHER METAL POWDERS (REF. 64)

	Bulk				-		
,	Density of	Weight of	Weight of	Average	Average	Density	Per Cent of
	Metal	Metal	Metal Powder/	Diameter of	Density of	of Solid	Theoretical
Metal	Powder,	Powder,	Weight of	Compacted	Compacted	Metal,	Density
Powder(a)	g/cc	g	Explosive	Mass, cm	Mass, g/cc	g/cc	Achieved
W-titanium(b)	1,53	675	11.2	3.5	4.0	4.5	89
Aluminum	1.29	57 5	9.6	3.8	2.7	2.7	100
Copper	5,25	2154	16.5	4.2	8.45	8.9	95
Iron	2.5	1080	8.3	3.2	7.65	7.9	97

⁽a) All powders - 60 mesh.

⁽b) A granular titanium obtained by the sodium-reduction process.

Pressureless Consolidation. The general topic of pressureless consolidation of metal powders has been discussed in detail by Hausner (Ref. 63). Of the two principal methods of forming powders without applied pressure, slip casting is not well adapted to titanium powder because of the presence of embrittling reagents used in forming the powder slip. It is possible that the second method, loosepowder sintering, might be useful for porous-structure preparation. In Soviet work, titanium powder was compacted to 38 per cent of full density by vibration (Ref. 65). The vibrator used had a frequency of 14,000 cycles per minute and amplitudes up to 10 microns.

TITANIUM-BASE ALLOYS

Powder metallurgy has been employed by numerous investigators in making a wide range of titanium-alloy parts (Refs. 39-42,66-76). In most of their work, the Soviets have used calcium-reduced titanium (Refs. 66,72,75,76), although calcium-reduced metal is ordinarily excessively high in oxygen content. The consolidation procedures used in some of the more recent work in making alloy parts are summarized in Table XXV. In practically every instance, alloys were made from elemental powders. In one case, a titaniumaluminum master alloy powder was used. Tables XXVI and XXVII from Weber (Ref. 41) illustrate the properties of Ti-2Al and Ti-6Al-4V alloys as influenced by pressing pressure. As in the case with unalloyed titanium, the rate of improvement in properties with increasing pressure levelled off at about 50 tsi. Figure 30 illustrates the strengths achieved in powder-metal sinterings. The fourth alloy in the figure (4Al-4Mn) shows what can be achieved if coining and resintering are added to the processing. Although this material was sintered at a lower temperature than the first three alloys, the final strengths were comparable to those of arc-melted and wrought alloys. Ductility, impact, and fatigue strengths were also comparable to arcmelted and wrought alloy. Figure 31 from Grimwade (Ref. 67) shows the superior strength of a sintered and forged Ti-4Al-4Mn alloy as compared with a similar cast and wrought alloy. Tables XXVIII and XXIX, from this same paper, summarize room-temperature mechanical properties of the as-sintered alloy in various heat-treated conditions, and compares these with properties of the sintered and forged alloy. In general, the as-sintered alloys displayed low levels of tensile ductility and strength. The increments of improvement achieved by forging were appreciable.

TABLE XXV. SUMMARY OF PRESSING AND SINTERING SCHEDULES USED IN THE PRODUCTION OF A NUMBER OF ALLOYS

		Pressing Pressure.	
Source	Alloy	tsi	Remarks
Robins, Pitkin, and Jenkins	Ti-0 to 10Cr	40	1200 C (2190 F), 4 hours, vacuum press,
(Ref. 40)	Ti-0 to 10Mo	40	resinter; repeat sinter and press; final sinter 1200 C, 4 hours, vacuum
Weber (Ref. 41)	Ti-2Al	32, 51, 58	1850 F (1010 C), 4 hours, vacuum
	Ti-6Al-4V	45, 51, 58	2200 F (1205 C), 4 hours, vacuum
Schwope (Ref. 39)	Ti-1Al	70	2200 F (1205 C), 1 hour, argon
•	Ti-2Al	70	2200 F (1205 C), 1 hour, argon
	Ti-2Al-5Sn	70	2200 F (1205 C), 1 hour, argon
	Ti-4Al-4Mn		1832 F (1000 C), 1 hour, argon coined and resintered
Smart and Ellwood (Ref. 69)	Ti-21/2	40-50(a)	1300 C (2370 F), 1 to 4 hours, vacuum
	Ti-5Sn	40-50	Ditto
	Ti-10Sn	40-50	19
	Ti-15Sn	40-50	
Grimwade (Ref. 67)	Ti-4Al-4Mn	40	1250 C (2280 F), 4 hours, vacuum

⁽a) Optimum.

TABLE XXVI. MECHANICAL AND PHYSICAL PROPERTIES OF PRESSED AND SINTERED 2 PER CENT ALUMINUM ALLOY (REF. 41)

	Pre	essing Pressure,	tsi
Property	32	51	58
Tensile Strength, psi	70,000	85,000	86,000
Yield Strength, psi (0.2% offset)	59,000	70,000	72,000
Elongation, per cent in 1 inch	9	12	14
Reduction in Area, per cent	10	16	20
Hardness, R _B	82	91	
Brinell, 500-kg load	109	130	
Impact Properties (V-Notch Charpy), ft-1b	3.0	5.0	
Fatigue Strength (Rotating Beam 10,000 Cycles			
per Minute) Endurance Limit, 10 ⁷ cycles			30,000
Endurance Ratio, per cent			35
Green Density, per cent of theoretical 0.162 lb/in. 3	87.5	94	95
Sintered Density, per cent of theoretical 0.162 lb/in.3	91.0	95	96.2
Coefficient of Thermal Expansion, RT to 500 F Avg,			
microinch per degree F		4.27	
Electrical Resistivity, ohm-cm 10 ⁻⁶		93	
Thermal Conductivity, cal sec ⁻¹ cm ⁻² cm C ⁻¹		0.025	

TABLE XXVII. MECHANICAL AND PHYSICAL PROPERTIES OF PRESSED AND SINTERED 6A1-4V ALLOY (REF. 41)

		Pressing F	ressure, ts	i
Property	45	51	58	Heat Treated(a)
Tensile Strength, psi	112,000	119,000	120,000	146,000
Yield Strength, psi (0.2% offset)	105,000	107,000	110,000	133,000
Elongation, per cent in 1 inch	6	6	6	4
Reduction in Area, per cent	7	9	9	7
Hardness, RC	21	22.6	23.5	
Brinell (3000-kg load)	217	229	229	
Impact Properties (V-Notch Charpy), ft-lb	5.7	8.5	11.0	
Fatigue Strength (Rotating Beam 10,000 Cycles				
per Minute) Endurance Limit, 10 ⁷ cycles			27,000	
Endurance Ratio, per cent			23	
Green Density, per cent of theoretical 0.160 lb/in. 3	91.3	93.2	93.2	
Sintered Density, per cent of theoretical 0.160 lb/in. 3	95	96	96	
Coefficient of Thermal Expansion, RT to 500 F Avg,				
microinch per degree F	4.11		5.15	
Electrical Resistivity, olum-cm 10-6		180		
Thermal Conductivity, cal sec ⁻¹ cm ⁻² cm C ⁻¹		0.015		

⁽a) Heat treated 1 hour at 1750 F, water quenched, aged 24 hours at 900 F.

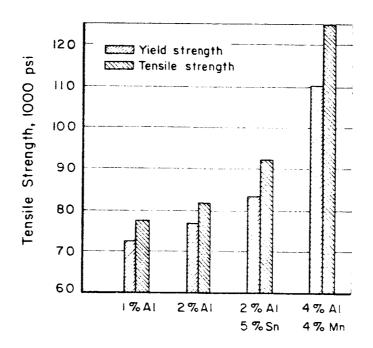


FIGURE 30. STRENGTH PROPERTIES OF TITANIUM ALLOYS (REF. 39)

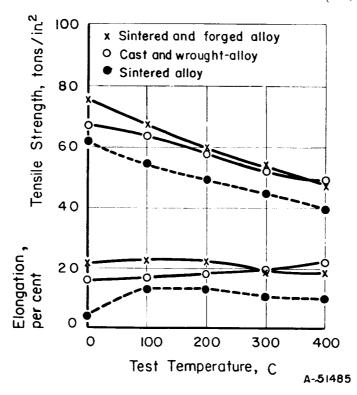


FIGURE 31. COMPARISON OF THE MECHANICAL PROPERTIES OF TI-4A1-4Mn ALLOY IN THE SINTERED, SINTERED AND FORGED, AND CAST AND WROUGHT CONDITIONS (REF. 67)

TABLE XXVIII. ROOM-TENIPERATURE MECHANICAL PROPERTIES OF SINTERED Ti-4Al-4Mn ALLOY IN VARIOUS HEAT-TREATED CONDITIONS (REF. 67)

			Tensile	Tensile Properties		
50 C 97.6 464 96.3 63.5 2.4 386 96.3 65.5 1.3 386 96.3 71.5 1.4 386 96.7 60.5 0.8 391 96.7 66.0 0.5 391 96.0 60.5 0 346 96.0 60.5 0 346 96.0 65.5 0 289 96.3 65.5 0 289 96.3 65.5 0 289 96.3 78.4 18.3 380	Condition	Density, per cent of theoretical	Tensile Strength, tsi	Elongation, per cent	Hardness, 50-kg load, DPH	Remarks
96.3 63.5 2.4 386 96.3 71.5 1.4 386 96.3 71.5 1.4 386 97.6 380 96.7 60.5 0.8 391 96.7 66.0 0.5 391 96.0 60.5 0 346 96.0 59.5 0 346 96.3 65.5 0 289 96.3 65.5 0 289 96.3 65.5 0 289 96.3 65.5 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Water quenched after 30 minutes at 1050 C	97.6	;	!	464	Solution treated in the eta field
96.3 71.5 1.4 386 97.6 380 96.7 60.5 0.8 391 96.7 66.0 0.5 391 96.0 60.5 0 346 96.0 59.5 0 346 96.3 65.5 0 289 96.3 60.0 0 289 96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Ditto, aged for 24 hours at 850 C	96.3	63. 5 65. 5	2.4	386 386	;
97.6 380 96.7 60.5 0.8 391 96.7 59.5 1.1 391 96.0 60.5 0 346 96.0 59.5 0 346 96.3 65.5 0 289 96.3 65.5 0 289 100 78.4 18.3 380	:	96.3	71.5	1,4	386	
0 C 96.7 60.5 0.8 391 96.7 59.5 1.1 391 96.7 66.0 0.5 391 0 C 60.5 0 346 96.0 59.5 0 346 0 C 96.3 65.5 0 346 100 78.4 18.3 380 100 76.5 18.3 380	Water quenched after 30 minutes at 880 C	97.6	;	;	380	Solution treated in the ($\alpha+\beta$) field
96.7 59.5 1.1 391 96.7 66.0 0.5 391 96.0 60.5 0 346 96.0 59.5 0 346 0 59.5 0 346 0 65.5 0 289 0 78.4 18.3 380 100 78.4 18.3 380	Ditto aged for 2 hours at 650 C	96.7	60.5	8.0	391	
96.7 66.0 0.5 391 96.0 60.5 0 346 96.0 59.5 0 346 0 to 950 C 96.3 65.5 0 289 96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Ditto	96.7	59.5	1.1	391	
0 C 96.0 60.5 0 346 96.0 59.5 0 346 0 to 950 C 96.3 65.5 0 289 96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380		96.7	66.0	0.5	391	!
0 to 950 C 96.3 65.5 0 346 0 to 950 C 96.3 65.5 0 289 96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Dirro aged for 8 hours at 750 C	0.96	60.5	0	346	
0 to 950 C 96.3 65.5 0 289 96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Ditto	96.0	59. 5	0	3+6	
96.3 60.0 0 289 100 78.4 18.3 380 100 76.5 18.3 380	Thermally cycled five times 900 to 950 C	96.3	65.5	0	588	;
100 78.4 18.3 380 100 76.5 18.3 380	Ditto	96.3	0.09	0	289	
100 76.5 18.3	Forged at 900 C and air cooled	100	78.4	18.3	380	Showing good ductility
	Ditto	100	76.5	18.3	380	

TABLE XXIX. MECHANICAL PROPERTIES OF SINTERED AND SINTERED AND FORGED Ti-4Al-4Mn ALLOY CREEP TESTED AT 200 AND 400 C (REF. 67)

						Tensile Pro	Tensile Properties After
unan Lagran	Creep-Test	Test Conditions		Young's Modulus, 1b/in. 2 x 10 ⁻⁶	Aodulus, x 10 ⁻⁶	Creep Tensile	Creep Testing
Condition	Load, tsi	Temperature, C	Min. Creep Rate, in./in./hr x 10-5	At Room Temperature	At Test Temperature	Strength, tsi	Elongation, per cent
As sintered	30	400	1.75	16.28	13.5	64.8	0.1
	20	400	0.083	17.2	13,75	73.2	0.4
	10	400	0.047	!	14.75	57.8	0.1
	40	200	0.005	17.35	14,72	1	;
Sintered and forged	Not tested	ested	;	;	;	74.4	15.0
)	30	400	1,11	17.00	11,93	80.7	6.4
	20	400	0.11	16,82	14.13	80.5	4.8
	10	400	0.053	16,00	14.28	81.0	9,15
	40	200	0.016	15.84	14.52	t -	•

INERT-DISPERSOID-STRENGTHENED TITANIUM

Powder-metallurgy technology in general provides the best procedures for incorporating "inert" reinforcement agents such as oxides, metal fibers, inorganic compound fibers, etc. (Refs. 39, 77-80). Figure 32 illustrates the strengthening of titanium by a TiC addition. The carbide averaged 5 microns in size. Cold-pressed compacts were vacuum sintered at 2200 F, canned, and heated to 1800 F for extrusion. Figure 33 illustrates the change in fiber orientation that takes place during the working of a discontinuous fiber composite. Figure 34 illustrates the strengthening of titanium by molybdenum fibers. Figures 35 to 38 provide additional data on fiber and dispersoid-strengthened titanium and a fiber-strengthened Ti-6Al-4V alloy.

ECONOMICS

Whether or not the powder-metallurgy consolidation and related processing are economically advantageous depends on numerous factors, especially the cost of powder. Figure 39 shows that the number of steps involved in arriving at a finished part are fewer and in some instances less costly by powder metallurgy than by the wrought-titanium route. Furthermore, the product yield per pound of material is much greater by powder metallurgy than for parts machined from wrought material. Tables XXX and XXXI illustrate cost savings for a number of bearing housings made by hot pressing followed by machining as compared with forging from bar stock followed by machining. In many parts that might be made by powder metallurgy no final machining would be required and the cost advantage would be correspondingly greater. Figure 40 illustrates several types of parts that have been produced economically by powder-metallurgy procedures.

SAFETY IN STORAGE AND HANDLING

There is general agreement that the handling of titanium in powder form does not present any physiological hazard such as that created by beryllium powder. There may exist, however, a very real fire and/or explosion hazard for powder having a high exposedsurface to volume ratio. For the combustion reaction $\text{Ti} + \text{O}_2 = \text{TiO}_2$, the heat of formation, $\Delta \text{H}_f^{\circ}$, amounts to -225,750 cal/mole at room temperature. This indicates the potential for generating intense heat if ignition should occur.

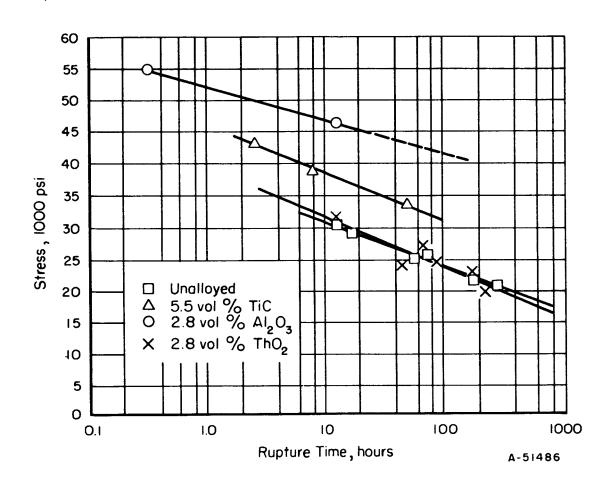


FIGURE 32. STRESS VERSUS LOG RUPTURE TIME AT 800 F RESULTING FROM DISPERSIONS OF VARIOUS COMPOUNDS IN TITANIUM (REF. 78)

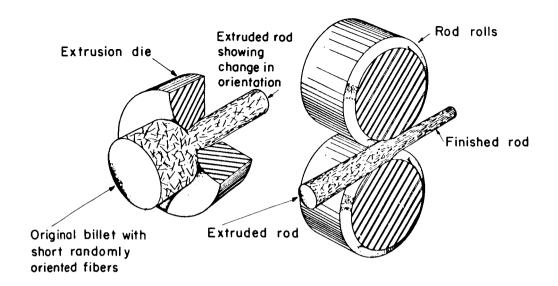


FIGURE 33. FABRICATION OF DISCONTINUOUS FIBER COM-POSITE, ILLUSTRATING THE CHANGE IN ORI-ENTATION RESULTING FROM EXTRUSION AND ROLLING (REF. 79)

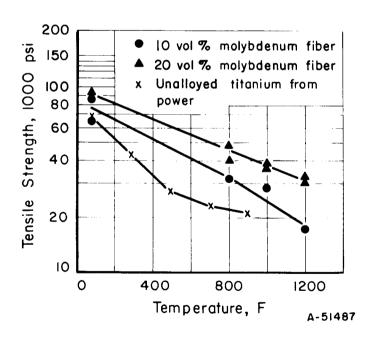


FIGURE 34. TENSILE STRENGTH OF DISCONTINUOUS FIBER-REINFORCED STRUCTURES IN UNALLOYED TITANIUM (REF. 79)

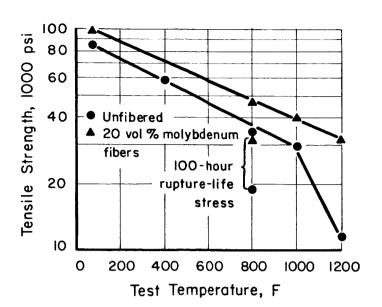


FIGURE 35. EFFECT OF TEMPERATURE ON TENSILE STRENGTH OF FIBERED AND UNFIBERED TITANIUM (REF. 39)

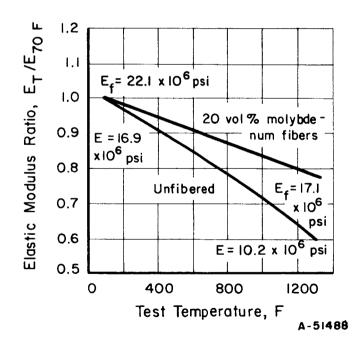


FIGURE 36. EFFECT OF TEMPERATURE ON ELASTIC MODULUS OF FIBERED AND UNFIBERED TITANIUM (REF. 39)

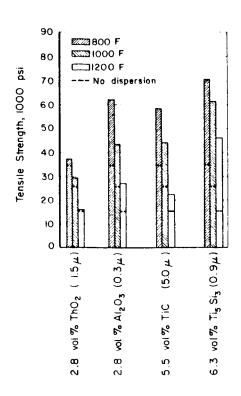


FIGURE 37. EFFECT OF TEMPERATURE ON TENSILE STRENGTHS OF DISPERSIONS IN TITANIUM (REF. 39)

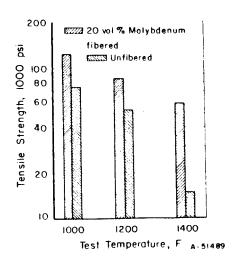


FIGURE 38. EFFECT OF TEMPERATURE ON TENSILE STRENGTH OF FIBERED AND UNFIBERED 90 PER CENT Ti-6A1-4V ALLOY (REF. 39)

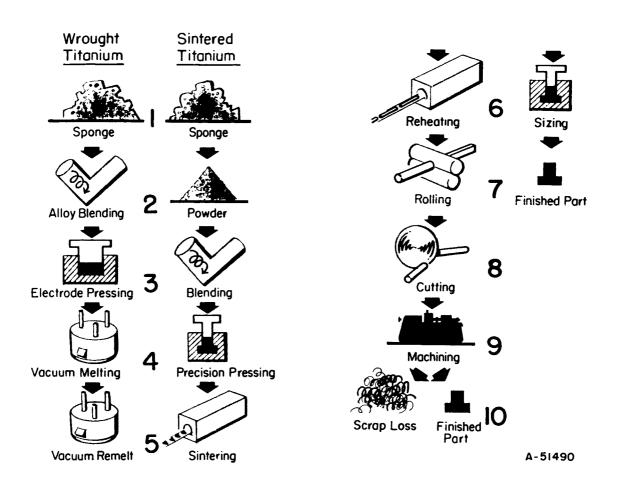


FIGURE 39. PROCESSING STEPS REQUIRED TO MAKE PARTS BY POWDER METALLURGY COMPARED WITH WROUGHT PRODUCTS

TABLE XXX. MATERIAL UTILIZATION FACTORS FOR HOT-PRESSED J73 BEARING HOUSINGS (REF. 46)

Part	Calculated Finished Part Weight, Ib	Hot-Sintered Blank Weight, 1b	Material Utilization(a), Hot Sintered	Forging Blank Weight, lb	Material Utilization(a), Forging
Α	0.31	1.00	3.23	2.0	6.42
В	0.12	0.58	4.82	0.75	6.22
С	0.34	1.00	2.94	1.12	3.28
D	0.19	0.92	4.84	1.38	7.28
E	0.23	0.81	3, 52	1.00	4.34
F	0.21	0.78	3.76	1.13	5.37
G	0.21	0.46	2.19	0.87	4.15
Н	0.42	0.62	1.48	0.87	2.06
I	0.30	0.51	1.70	0.62	2.06
J	0.57	1.06	1.86	1.50	2,63
K	0.24	0.88	3.67	1,19	4.86
L	0.24	0.90	3.75	1.13	4.91
M	0.16	0.63	3.94	0.81	5.06
N	0.23	0.65	2.82	1.00	4.35
0	0.72	2.30	3.20	8.87	12.30
P	0.18	0.73			

(a) Material utilization = $\frac{\text{weight of raw material required}}{\text{weight of finished part}}$.

TABLE XXXI. COST REDUCTIONS ON SEVERAL J73 BEARING HOUSINGS (REF. 46)

Part	Unit Price, Hot Pressed and Machined	Unit Price, Forged and Machined (Minimum)
Е	\$ 62 . 00	\$81.75
H	74.50	84.27
G	71.00	76.00
J	62.00	91.79
M	62.00	82,25

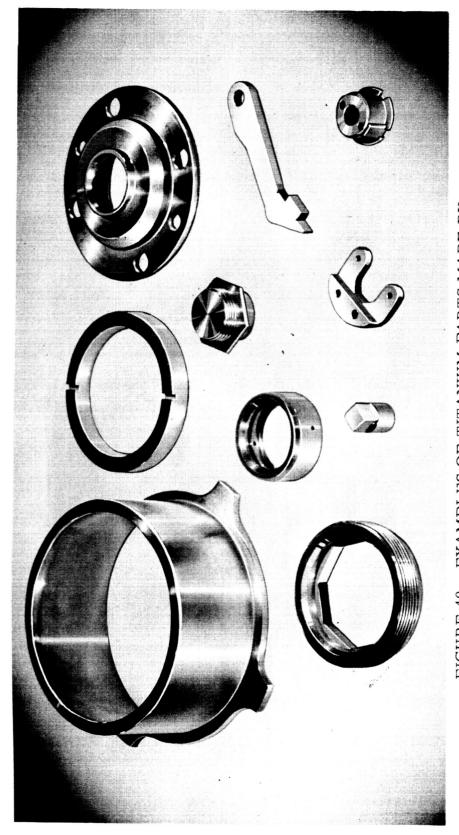


FIGURE 40. EXAMPLES OF TITANIUM PARTS MADE BY POWDER-METALLURGY PROCESSING

Two-thirds actual size.

Courtesy of Clevite Corporation.

Table XXXII from a recent U. S. Bureau of Mines summary (Ref. 81) lists titanium powder in the "severe" category with respect to ignition and explosibility along with a number of other metal powders. The hydride appears to be a little less dangerous in this regard.

TABLE XXXII. IGNITION TEMPERATURES AND EXPLOSIBILITY OF METAL POWDERS (REF. 81)

Material	Ignit Tempe Cloud	erature,	Minimum Explosive Concentration, oz/ft ³	Minimum Igniting Energy for Dust Cloud, millijoules	Maximum Pressure, psig	Maximum Rate of Pressure Rise, psi/sec	Index of Explosibility(a)
	 _		· · · · · · · · · · · · · · · · · · ·	Severe			
				00,010			
Aluminum, atomized Aluminum-	650	760	0.045	50	73	20,000+	>10
magnesium alloy	430	480	0.020	80	86	10,000	>10
Magnesium	620	490	0.040	40	90	9,000	>10
Thorium hydride	260	20	0.080	3	60	6,500	>10
Zirconium	20	190	0.045	15	55	6,500	>10
Uranium hydride	20	20	0.060	5	43	6,500	>10
Titanium	330	510	0.045	25	70	5,500	>10
Uranium	20	100	0.060	45	53	3,400	>10
Thorium	270	280	0.075	5	48	3,300	>10
				Strong			
Titanium hydride	480	540	0.070	60	96	12,000	6.0
Zirconium hydride	350	270	0.085	60	69	9,000	3.7
Aluminum -silicon							
alloy	670		0.040	60	74	7,500	3.6
Calcium silicide	540	540	0.060	150	73	13,000	2.0
Iron, carbonyl	320	310	0.105	20	41	2,400	1.6
Ferrotitanium	370	400	0.140	80	53	9, 500	1.3
Coal, Pittsburgh seam	610	180	0.055	60	83	2,300	1.0

⁽a) Index of explosibility = ignition sensitivity x explosion severity.

It is impossible to make quantitative generalizations about the inflammability of titanium powder, sponge, turnings, etc. The rate of burning is dependent on too many factors peculiar to any set of circumstances. As a rule, the finer the particle size, the greater the invitation to rapid combustion. Figure 41 (Ref. 81) illustrates this effect for aluminum powder and it can be inferred that titanium would be affected in a similar manner.

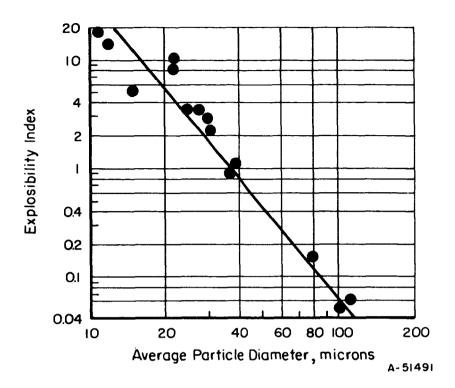


FIGURE 41. EFFECT OF AVERAGE PARTICLE DIAMETER OF ATOMIZED ALUMINUM ON EXPLOSIBIL-ITY INDEX (REF. 81)

Important safeguards in the handling and storage of titanium and other metal powders include: elimination of all possible ignition sources near the storage and processing areas; use of an inert-gas atmosphere where practical; reduction in the amount of fine-dust production, as far as possible; and good housekeeping. The sub-division of large batches of powder into smaller isolated lots may be advisable. If the powder is produced wet, it should be thoroughly dried before storage. If an explosion hazard cannot be avoided, the surrounding structure should be well vented. The Bureau of Mines suggests that anyone working with fine titanium powder should follow the latest recommendations outlined by the National Fire Protection Association. When titanium powders are shipped, Interstate Commerce packaging specifications should be followed.

SHAPING BY SPRAYING

In recent years there has been considerable activity in spraying a variety of metals and ceramic materials. Spraying provides a means for applying thin coatings for improved resistance to wear, oxidation, corrosion, and erosion, and for restoring worn areas on parts of considerable value. A list of spray materials and substrates either of current interest or of potential interest is given in Table XXXIII (Ref. 82).

For spraying to be of interest in making massive parts, it is essential that the item be of considerable value, be of relatively simple shape, and require a material that is not readily cast or machined. There are a few instances where these conditions exist, notably rocket-nozzle inserts and nose cones, but for these items, tungsten or high-melting compounds are the preferred materials.

Titanium and titanium alloys are not good candidates for spraying into massive shapes because they can be processed easier by more conventional and less costly methods. On the other hand, spraying for providing a thin coating of titanium or to build up a localized area on a valuable titanium part may be of interest.

TYPE OF EQUIPMENT REQUIRED

Because molten titanium is very reactive, it is necessary that it be kept out of contact with oxygen, nitrogen, or carbon if serious contamination is to be avoided. Therefore, only spraying methods employing an inert gas can be used. Plasma spraying, using argon atmosphere, is a suitable method for spraying titanium (Refs. 82-84). The plasma torch is a gas-stabilized arc device. A pressurized gas flows into a plenum chamber where it is ionized between a tungsten electrode and a water-cooled copper nozzle that serves as the other electrode. As the ionized gas flows into the reduced section of the nozzle it becomes highly concentrated, resulting in a further increase in temperature. There also is a pinch effect that serves to concentrate the current in the central region of the plasma. Self-induced magnetic fields constrict the plasma further. These combined effects result in temperatures in excess of 15,000 F.

A schematic drawing of a typical plasma spray gun is shown in Figure 42. The material to be sprayed is injected into the plasma stream as a powder or as an automatically fed wire. The molten

TABLE XXXIII. SPRAY MATERIALS AND SUBSTRATES FOR POTENTIAL PLASMA-SPRAY APPLICATIONS (REF. 82)

	Nitrides, silicides,					
Oxides	and Sulfides	Carbides	Borides	Metals and Alloys	Cermets and Composites	Substrates
Al ₂ O ₃	Si ₃ N ₄	TiC	TiB	Cr, Fe	Tic Cr	Metals and alloys
Ca0				Co, Cu	$TiB_2 \nearrow + \ Ni$	Ceramics
/ MgO	ZrN	$_{ m B_4C}$	${ m TiB}_2$	Ti	$Z_{\Gamma B}$	Plastics
ZrO_2 Y_2O_3				Th	Haynes LT	Steels
$ \operatorname{ZrO}_2 \cdot \operatorname{SiO}_2 $	Tin	MC	ZrB	W, Ta, Cb	Fe	Stainless steel
SiO_2				Mo, Nb, Re	Ü	Inconel
BeO	MoSi ₂	$TiC + B_4C$	MoB	Ni, Monel	Ni	Kovar
$50\% \text{ TiO}_2 + \text{Al}_2\text{O}_3$				Cd	_	Molybdenum
$A_{12}O_{3} + S_{10}O_{2}$	MoS_2	HfC	ZrB_2	$C_{\mathbf{r}} + N_{\mathbf{i}} + B$	Si	Aluminum
Mixed Oxides	ı			Coast Metals,	√ _{Mo}	Silicon
Gd ₂ O ₃	$CrSi_2$	TaC	B + metal	Nos. 63, 54, 55, 56	40Co + ZrO ₂	Magnesium
Oxide + metal	ı		mixtures	Si	WC + 12% Co	Beryllium
mixtures	${ m TiSi}_2$	ZrC		В	$40Ni + Al_2O_3$	Copper
$1 \text{ ThO}_2, \text{ Y}_2\text{O}_2$			CrB	Sn	$Z_1O_2 + 40\%$ Co	Zirconium
nos		Cr_3C_2		Stainless steels	$Al_2O_3 + 40\%$ Ni	Graphite
$ $ HfO $_2$			CrB_2	Stellite 1	60CrC-Co	Oxides
MgO		CbC		Stellite 6	Moly + Mn mixtures	High-temperature plastics
$ $ TiO $_2$				Miscellaneous alloys	Kenface + 40%	Fused silica
R. E. oxides				Colmonoy 6	Colmonoy 6	
CeO ₂				Au, Ag		
Porcelain powder				Pt, Pd		
Glass (fixed m p)				Zn		
Ba TiO ₃				Inconel		
MgO.Al ₂ O ₃				Al		
,				Be		
				Zr		
				80Ni-20Cr		
				Brass, bronze		
				Haynes alloys		
				Nicrobraze		
				Hastelloy C		

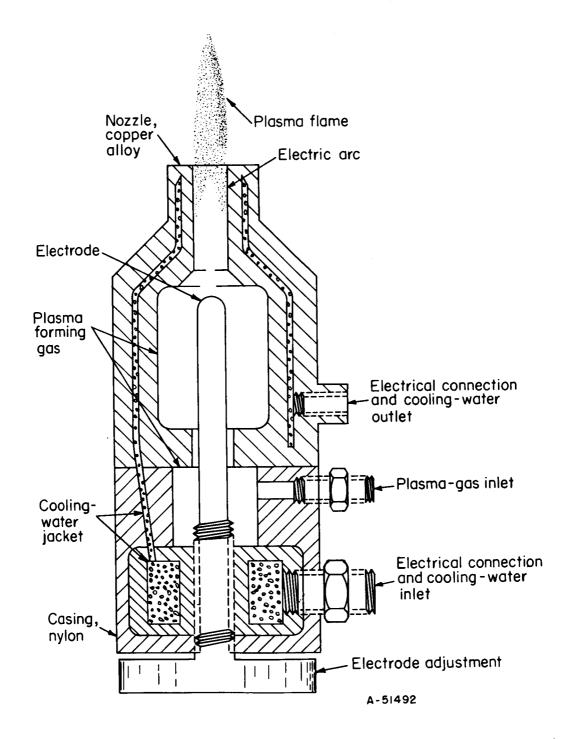


FIGURE 42. SCHEMATIC OF A TYPICAL NONTRANSFERRED ARC TYPE OF PLASMA-ARC TORCH EMPLOYED FOR METAL-SPRAYING APPLICATIONS (REF. 83)

particles strike the surface of the work piece at high velocity and adhere mainly as the result of mechanical bonding.

Another process for spraying titanium and other reactive metals under protective atmospheres was described by W. E. Stanton (Ref. 85). The metal to be sprayed, in the form of 3/16-inch diameter wire, was fed into an induction coil by a pair of rollers driven by an electric motor. A wire straightener was incorporated in the wirefeeding mechanism to ensure true alignment of the wire with the axis of a nozzle. As the wire emerged from the feed rollers, it first passed through a system of gas seals and then through the center of a nonmetallic nozzle. The nozzle could be of alumina, porcelain, or even certain plastics. The nozzle extended into the induction coil for a distance of about 3/16 inch and continuous melting of the wire occurred at a distance of 3/8 inch from the nozzle tip. The molten metal was atomized and sprayed by a stream of argon in an inert-gas chamber. Photomicrographs of titanium deposits made by the process showed an acicular structure. No mechanical-property data were reported.

STATE OF THE ART

A review of published literature and unpublished reports from 1958 to 1965, and contacts made with people active in the metal-spraying field (Refs. 86-89), revealed that there has been very little interest in spraying titanium.

Plasma flame spraying of titanium coatings was discussed in a paper by H. S. Ingham, Jr. (Ref. 90). Titanium hydride powder was sprayed onto smooth surfaces of high-density Alundum and zirconium oxide with excellent bonding. The titanium hydride powder was -170 +325 mesh and contained approximately 3.4 per cent hydrogen by weight. Titanium hydride is not pyrophoric, and can be handled in air. Titanium metal, on the other hand, is pyrophoric in sizes much below 200 mesh.

Titanium hydride was sprayed with both the Metco Thermo Spray gun using either acetylene or hydrogen with oxygen and the Metco 2MB plasma flame spray gun using nitrogen-hydrogen gas. Resulting coatings were metallic in appearance and were believed to be metallic, since spraying was done at a temperature well above the decomposition temperature for titanium hydride. However, metallographic examination revealed 5 to 10 per cent oxides for the method employing oxygen.

POSSIBLE APPLICATIONS

Possible applications for sprayed titanium include coatings for corrosion resistance and for metal-to-ceramic seals. Buildup on titanium parts for change of contour or restoration of worn areas is also a possible application. To date these potential applications have stimulated only limited development in the art of spraying titanium.

SHAPING BY ELECTROFORMING

Electroforming provides a method for fabricating complex shapes in one piece with good dimensional accuracy, surface finish, and chemical homogeneity. Typically, electroforming requires the fabrication of a mandrel, the electrodeposition of a metal on the mandrel, and the removal of the mandrel from the electrodeposited metal by pulling, prying, melting, or dissolving. Structures with good strength and density are being produced by electroforming of nickel, nickel-cobalt alloys, iron, and copper, using aqueous solutions (Ref. 91).

Attempts to deposit dense, coherent titanium were unsuccessful, until Solar Aircraft Company devised a high-temperature, fused-salt bath and adopted steel or stainless steel mandrels that would resist the salt mixture. A. R. Stetson described the electrodeposition procedure for titanium in a recent publication (Ref. 92). A eutectic mixture of 91 per cent potassium titanium chloride and 9 per cent sodium fluoride was maintained at 1400 to 1740 F in graphite containers and operated with cathode current densities of 15 to 25 amp/ft² (4 volts). The deposition rate gradually decreased from 2 to <0.5 mil/hour as thickness increased to >30 mils. The mandrels were dissolved in solutions containing sulfuric and nitric acid, after electrodeposition. Hollow titanium cylinders and vessels with one closed end were produced at Solar (Ref. 93). No property data are available for electroformed titanium, nor have other organizations reported success in electroforming titanium.

It now appears that activity in electroforming titanium has been dropped because other methods of fabricating titanium are easier to accomplish. The high temperature required for electrolysis of titanium-salt solutions and the cost of the high-temperature-resistant mandrels have discouraged research and development. It is understood, however, that work is continuing on the electrodeposition of thin titanium coatings for corrosion protection. Union Carbide

Corporation (Cleveland, Ohio) has used the fluoride-chloride eutectic reported by Stetson (Ref. 94). Fused chloride salts have been used at the U. S. Bureau of Mines (Ref. 95).

SHAPING BY CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition consists of causing molecules in the vapor phase to react chemically or at a heated surface. The reaction and conditions are so chosen that all of the products except the desired solid are volatile at the processing temperature. Atoms or molecules of the solid are added by means of the reaction one at a time so that, initially at least, the shape of the deposit conforms to the shape of the deposition surface. In most of the reactions of this type studied to date the shape of the final deposit is incidental to the primary goal of producing a pure solid, providing a protective coating for the surface, etc. However, the molecular forming nature of the process does indeed hold promise that desired final shapes of many different materials may be fabricated through chemical vapor deposition on suitable mandrels.

A general description of chemical vapor deposition as well as detailed discussion of some specific areas of application is given in a report prepared by J. M. Blocher, Jr., and others (Ref. 96). One chapter of a forthcoming publication (Ref. 97) deals with vapor forming and joining. In general, a suitable substrate is heated (resistively, by induction or by radiation) within a reaction chamber and exposed to the feed vapor (metal halide, carbonyl, metal-organic, etc.). In a closed system the reactant and product molecules move to and from the surface by diffusion, while in a flow system the products are continually removed as fresh feed arrives at the surface. Alloys can be deposited by feeding a mixture of metal-bearing vapors.

Titanium can be deposited by thermal decomposition of titanium tetraiodide or by the hydrogen reduction of titanium tetrabromide at temperatures from 1832 to 2552 F. Dense microcrystalline deposits can be obtained. The approach to fabrication of desired shapes would be to use a preformed mandrel as the deposition surface that could then be removed by melting, leaching or other means. The principal problems to be overcome relate to control of thickness through regulation of the rate of deposition over all the surface, and control of the nucleation and growth to obtain the desired morphology. No information was found relative to the use of chemical vapor deposition to form titanium or titanium-alloy bodies. The chief advantage of

shaping by chemical vapor deposition would best be realized in forming of parts having complex shapes of materials that are difficult to fabricate by other methods. Thus, titanium is not a likely candidate for making shapes by vapor deposition.

CONCLUSIONS AND RECOMMENDATIONS

SHAPING BY CASTING

The high melting temperature of titanium and the chemical reactivity of molten titanium require special melting and molding techniques that place restrictions on the quality of the castings and contribute to the high cost of castings. Castings of higher quality and of lower cost might be expected if marked improvement could be made in the following areas:

- (1) A molding process that is simpler and quicker than the present rammed-graphite molding process
- (2) A molding formulation that is more inert than graphite to chemical reaction with the melt, chills the melt less drastically than a rammed-graphite mold so that more intricate shapes can be run with a better finish and better reproduction of surface detail, and produces castings having narrow and reproducible dimensional tolerances
- (3) A core-molding formulation having the characteristics given in Item 2 but, in addition, having the characteristics of easier and quicker removal from the casting
- (4) A method of melting that provides a desired volume of metal at a specified uniform degree of superheat and that can be poured at a desired rate. The present skull-melting furnace produces a melt that is not uniform in temperature during pouring. Because it must be poured at the highest possible rate, a portion of the melt at excessive superheat can aggravate reaction with the mold, insufficient superheat can result in a misrun or in poor feeding of the solidification shrinkage, and excessive erosion of the mold can occur from the rapid pouring.

All of the above problem areas are important to the improvement of the quality and the cost of producing titanium castings. Their solution will require ingenious approaches that have not yet been developed.

SHAPING BY POWDER METALLURGY

Of all the problems with titanium powder metallurgy one problem stands out significantly, namely, providing a less expensive source of high-quality powder. The problem of obtaining good powder at economical prices is more severe in the case of titanium than, for example, in the case of iron or copper. It has been shown that the production of titanium hardware by the powder route is not only economically but also technically advantageous in numerous instances, that is if the starting material were available at a reasonable cost. It is difficult to quote a fixed breakeven figure for powder costs. At the present time, this figure appears to be about \$2.00/lb. The use of cheaper but less pure grades of powder is less feasible in the case of titanium than with many other metals because no purification is possible during subsequent consolidation, e.g., by the hydrogen reduction or vacuum elimination of oxide contamination.

A second problem area is in the development of good dispersion-strengthened titanium-base alloys. The powder-metallurgy approach to the production of such alloys would be justified in view of the difficulty or the impossibility of making this type of material by a melting and casting procedure. The development of SAP-type alloys has created a considerable amount of interest in analogous structures in other systems. Present titanium alloys function quite well up to about 800 F, but above this temperature a rapid decrease in strength occurs. A direct parallel between SAP and titanium is not possible because oxygen is very soluble in titanium and causes embrittlement. Some preliminary work has been done on the incorporation of ThO2 in titanium. The success obtained with thoriated nickel has not been achieved, however, in the case of titanium. The development of fiber-reinforced titanium also appears to represent an area that merits further effort.

SHAPING BY SPRAYING

The high affinity of molten titanium and titanium alloys for gaseous contaminants makes spraying with a high-purity nonreactive

gas, such as argon, essential. Melting can be accomplished in a plasma or, if titanium wire is used, an induction coil may be employed. Further development work is needed on spraying equipment and on the nature of the deposit, if the process is to find significant application.

SHAPING BY ELECTROFORMING

The high temperatures required for deposition of titanium from fused salts and the high cost of the mandrels make electroforming of titanium shapes impractical at the present time. Therefore, research leading to lower temperature baths and less expensive mandrels may be warranted.

SHAPING BY CHEMICAL VAPOR DEPOSITION

The relatively high temperatures required for the chemical vapor deposition of titanium places stringent requirements on the material chosen for the mandrel. Research is required to develop a material that can be easily machined, does not react with titanium at deposition temperatures, and is capable of being stripped subsequent to the vapor-forming process.

The preparation of high-purity titanium can now be carried out by means of well-developed techniques. However, the morphology of the deposit has not been an important specification to date. In vapor forming, the morphology becomes a prime consideration. The questions of how the nucleation and growth processes determine final morphology, and how to influence the nucleation and growth so as to obtain the desired morphology must be answered by careful study of these fundamental processes.

APPENDIX

SPECIFICATIONS COVERING CAST TITANIUM AND TITANIUM ALLOYS

TENTATIVE SPECIFICATION FOR TITANIUM AND TITANIUM ALLOYS CASTINGS $^{\mathrm{l}}$

ASTM Designation: B 367-61 T

Issued, 1961.²

This Tentative Specification has been approved by the sponsoring committee and accepted by the Society in accordance with established procedures, for use pending adoption as standard. Suggestions for revisions should be addressed to the Society at 1916 Race St., Philadelphia 3, Pa.

Scope

1. This specification covers three grades of annealed titanium and titanium alloy castings as follows:

Grade C-1. - Unalloyed titanium.

Grade C-2. - Titanium alloy (6 per cent aluminum, 4 per cent vanadium).

Grade C-3. - Titanium alloy (5 per cent aluminum, 2.5 per cent tin).

Basis of Purchase

- 2. Orders for material under this specification shall include the following information as applicable:
 - (1) Grade number (Section 1),
 - (2) Size of tension test specimens (Section 9),
 - (3) Nondestructive test requirements (Section 11),
 - (4) Finish (Section 13),
 - (5) Marking (Section 14),
 - (6) Certification reports (Section 15), and
 - (7) Disposition of rejected material (Section 16).

Manufacture

3. The titanium castings covered by this specification shall be manufactured by the methods conventionally used for reactive metals.

¹Under the standardization procedure of the Society, this specification is under the jurisdiction of the ASTM Committee B-2 on Nonferrous Metals and Alloys.

²Accepted by the Administrative Committee on Standards, May 10, 1961.

Specification for Titanium Alloy Castings (B 367)

Chemical Composition

4. The grades of titanium and titanium alloy castings covered by this specification shall conform to the requirements as to chemical composition prescribed in Table I.

Sampling for Chemical Analysis

5. Samples for chemical analysis shall be representative of the material being tested. The utmost care shall be used in sampling titanium for chemical analysis because of its great affinity for elements such as oxygen, nitrogen, and hydrogen. Chips should be collected from clean metal and tools shall be clean and sharp.

Methods of Chemical Analysis

6. The chemical analysis shall be conducted in accordance with the Methods for Chemical Analysis of Titanium and Titanium Base Alloys (ASTM Designation: E 120), 3 or as agreed upon by the manufacturer and the purchaser.

Check Analysis

7. Check analysis tolerances, Table II, do not broaden the specified heat analysis requirements, but cover variations between different laboratories in the measurement of chemical content. The manufacturer shall not ship material that is outside the limits specified in Table I for the applicable grade. Check analysis tolerances shall be as specified in Table II.

Tensile Properties

- 8. (a) Castings supplied under this specification as represented by test specimens shall conform to the requirements for tensile properties prescribed in Table III for the grade specified.
- (b) Tension test specimens shall be machined and tested in accordance with the Methods of Tension Testing of Metallic Materials (ASTM Designation: E 8). ⁴ Tensile properties shall be determined using a strain rate of 0.003 to 0.007 in. per in. per min through the specified yield strength.

³1960 Book of ASTM Methods for Chemical Analysis of Metals.

⁴¹⁹⁶¹ Book of ASTM Standards, Part 3.

TABLE I. CHEMICAL COMPOSITION REQUIREMENTS

Element	Grade C-1	Grade C-2	Grade C-3
Nitrogen, max, per cent	0.05	0.07	0.07
Carbon, max, per cent	0.10	0.10	0.10
Hydrogen, max, per cent	0.0100	0.0100	0.0100
Iron, max, per cent	0.40	0.40	0.50
Oxygen, max, per cent	0.40	0.25	0.30
Aluminum, per cent		5.5 to 6.5	4.0 to 6.0
Vanadium, per cent		3.5 to 4.5	
Tin, per cent			2.0 to 3.0
Titanium, per cent ^(a)	remainder	remainder	remainder

(a) The percentage of titanium is determined by difference.

TABLE II. CHECK ANALYSIS TOLERANCES

Element	Maximum or Range, per cent	Tolerance, per cent
Nitrogen	0.07	+0.02
Carbon	0.10	+0.02
Hydrogen	0.010	+0.002
Iron	0.50	+0.15
	0.25	+0.04
Oxygen	0.30	+0.06
	0.40	+0.08
Aluminum	4.0 to 6.5	±0.40
Vanadium	3, 5 to 4.5	±0.15
Tin	2.0 to 3.0	±0.1 5

TABLE III. TENSILE PROPERTIES

Grade	Tensile Strength, min, psi	Yield Strength (0.2 Per Cent Offset), min, psi	Elongation in 2 In., min, per cent
C-1	65 000	55 000	12
C-2	130 000	120 000	6
C-3	115 000	105 000	8

Specification for Titanium Alloy Castings (B 367)

Test Specimens

9. All test specimens shall be cast from the same heat at the same time and in the same manner as the castings they represent. The bars shall be of sufficient size to be machined into a 0.250-in. diameter test section, having a 1-in. gage length, in accordance with Fig. 8 of Methods E 8. Other size test bars may be specified by the purchaser and agreed upon by the manufacturer.

Number of Tests

10. Two tension specimens shall be tested for each heat of material.

Nondestructive Inspection

- 11. (a) The manufacturer shall inspect such castings by radiographic or other methods of nondestructive inspection if specified in the contract or purchase order and when mutually agreed upon by the manufacturer and the purchaser.
- (b) Methods of procedure and the number of pieces and areas to be inspected shall be as agreed upon by the manufacturer and the purchaser.

Workmanship

12. All castings shall be made in a workmanlike manner and shall conform to the dimensions on drawings furnished by the purchaser before production of parts is started. If the pattern is supplied by the purchaser, castings shall conform to the dimensions predicated by the pattern. The castings shall be free from injurious external and internal imperfections of a nature that will interfere with the purpose for which the castings are intended.

Finish

- 13. (a) Castings shall be cleaned as agreed upon by the manufacturer and the purchaser. Cleaning may be accomplished by blasting with grit or any metallic corrosion-resisting shot or by any other approved method.
- (b) Repair by Welding. Minor defects that will not ultimately impair the usefulness of the castings may be welded by an inert-gas shielded process agreed upon by the manufacturer and the purchaser. The composition of the deposited metal shall approximate that of the

Specification for Titanium Alloy Castings (B 367)

casting itself, otherwise, the composition shall be subject to agreement between the manufacturer and the purchaser. Defects shall be considered minor when the depth of the cavity prepared for welding is not greater than 20 per cent of the actual wall thickness but in no case greater than 1 in. Minor defects may be welded without securing the approval of the purchaser, whereas defects other than minor may be repaired only with the consent of the purchaser. All castings shall be annealed following welding.

Marking

14. Marking shall be as agreed upon by the manufacturer and the purchaser.

Certification

15. If so requested by the purchaser, the manufacturer shall supply at least one copy of his report certifying that the material supplied has been inspected and tested in accordance with the requirements of this specification and that the results of chemical analysis and mechanical tests meet the requirements of this specification for the appropriate grade.

Rejection

16. Material not conforming to this specification or to authorized modifications shall be subject to rejection. Unless otherwise specified, rejected material may be returned to the manufacturer at the manufacturer's expense, unless the purchaser receives, within three weeks of notice of rejection, other instructions for disposition of the material.

OREGON METALLURGICAL CORPORATION MATERIAL SPECIFICATION OMC-105

CASTINGS - UNALLOYED TITANIUM

1. SCOPE

This specification is primarily for corrosion-resistant, weldable, unalloyed titanium castings.

2. MATERIAL AND PROCESS

- 2.1. When titanium sponge is used as the starting material, the sponge shall be double vacuum melted before casting.
- 2.2. Unalloyed titanium solids and/or chips may be used as the starting material. Appropriate processes will apply when these materials are used.
- The final melting prior to casting shall be by the vacuum consumable-electrode process.

3. CHEMICAL COMPOSITION (See para. 7)

3.1. The chemical requirements are:

Carbon 0.10 max 0.015 max Hydrogen 0.05 max. Nitrogen Oxygen 0.40 max. (1) 0.40 max. Iron Other Elements, total 0.40 max. (2)

Titanium Balance

- (1) Excess of this limit shall not be cause for rejection.
- (2) Need not be reported.

4. MECHANICAL PROPERTIES (See para. 7.)

4.1. With the rate of strain maintained at 0.005 in. per in. per minute through the yield strength and increased so as to produce failure in approximately a minute after the yield strength is reached, the test bars produced with the casting shall have the following properties in the specified ranges.

> Tensile strength 65,000-105,000 psi Yield strength at 0.2% offset 55,000-95,000 psi 12% min. Elongation

OMC-105

4. MECHANICAL PROPERTIES (continued)

4.2. Five Brinell Hardness (3000 Kg) impressions per heat shall be made on the castings, the test plugs, or representative pieces from each pour. The average of the five hardness readings shall not exceed 235 BHN. No single hardness reading shall exceed 245 BHN.

5. QUALITY

- 5.1. Casting shall be uniform in quality and condition.
- 5.2. The surface shall be compatible with the casting process.
- 5.3. Weld repairs may be made when casting flows are deemed detrimental for final usage. Random shrinks and/or porosities characteristic in all castings may be accepted if they are not gross or do not affect the final usage.
- 5.4. Castings shall be dye penetrant inspected. Any linear indication where the length is four times or greater than the width will be removed or repaired.

6. IDENTIFICATION

- 6.1. If specified, each casting shall be identified with the part number and an Oremet identification symbol by the use of raised numbers in a location indicated on the drawing.
- 6.2. If specified but no location is shown on the drawing, the number shall be so located as not to be machined off in finishing to the required final dimensions.

7. REPORTS

7.1. Certified chemical and mechanical test results are reported upon request and at no additional cost.

The certification shall include the chemical test results, mechanical test results, the Oremet heat number, the quantity of castings, the casting part numbers, and the purchase order number.

OREGON METALLURGICAL CORPORATION MATERIAL SPECIFICATION OMC-164-B

CASTINGS - TITANIUM, 6-ALUMINUM, 4-VANADIUM - CERTIFIED

1. ACKNOWLEDGMENTS

1.1. OREMET shall mention this specification number in all pertinent quotations and when acknowledging purchase orders.

2. APPLICABLE SPECIFICATIONS

- 2.1. The following specifications, of the issue in effect on date of invitation for bids, form a part of this specification to the extent herein described:
 - 2.1.1. MIL-1-6865 Inspection, Radiographic
 - 2.1.2. MIL-1-6866 Inspection, Penetrant
 - 2.1.3. MIL-C-6021 Castings, Classification and Inspection
 - 2.1.4. Federal Test Method Standard No. 151
 - 2.1.5. X-ray Standard for Titanium Castings (Being prepared)

3. APPLICATION

3.1. This specification is primarily for high strength titanium alloy aircraft castings requiring room temperature ultimate tensile strength above 137,000 psi, lightweight, and good corrosion resistance.

4. TYPES AND GRADES

- 4.1. Unless otherwise specified, castings are to be in the ascast condition. If annealed condition is specified the annealing heat treatment shall be 1000°F for 4 hours followed by air cool.
- 4.2. Casting classification shall be as specified on the applicable casting grawing. Class definitions shall be as specified in MIL-C-6021.

CASTING METHOD

- 5.1. Casting molds shall be rammed graphite mixed with suitable binders, unless otherwise specified.
- 5.2. Melting shall be by the vacuum double melt process when the titanium source is either raw sponge or raw sponge compacts. Use of titanium solids in preparation of electrode stock is permitted, provided all other requirements of this specification are met. All melting shall be by the vacuum consumable electrode process.

6. COMPOSITION

6.1. Castings shall be of the following composition:

	Weight Percent
Carbon	$.10~\mathrm{max}$
Hydrogen	$.015 \mathrm{max}$
Nitrogen	.07 max
Oxygen	$.25~\mathrm{max}$
Iron	.30 max
Aluminum	5.5 - 6.5
Vanadium	3.5 - 4.5
Other Elements	.4 max
Titanium	Balance

6.2. Each heat shall be analyzed for each of the elements listed in paragraph 6.1. except titanium. Chemical analysis of each lot shall be certified by OREMET. Analysis for hydrogen shall be on samples removed after all vendor processing. All analyses shall be performed using equipment and procedures approved by the procuring agency. Hydrogen analysis sample shall be removed from a location designated on the casting drawing, or from a separate coupon from the same heat and processed at the same time as the casting lot. This coupon shall be no thicker than the thinnest section of the casting.

7. QUALITY

7.1. Castings shall be uniform in quality and condition, well cleaned, and have a uniformly smooth surface compatible

7. Quality (continued)

with the casting process. Castings shall be free of surface contamination (such as oxygen, nitrogen, or other foreign contaminants).

- 7.2. Unless otherwise specified, metallic grit or shot shall not be used for final cleaning.
- 7.3. Castings shall not be repaired by plugging, welding, peening, or other methods without written permission of the procuring agency.
- 7.4. The areas of castings subject to soundness requirement shall be as specified, and the number and extent of defects in such areas shall not be greater than indicated by the standard furnished or approved by the procuring agency. Combinations of cracks, shrinkage cavities, cold shuts, misruns, or other defects not individually cause for rejection, but which are so aligned as to cause stress concentration are cause for rejection.
- 7.5. When soundness is specified in accordance with paragraph 7.4 it shall be determined in accordance with visual, penetrant, and radiographic inspection methods established by MIL-C-6021, MIL-1-6865, and MIL-1-6866.

8. TENSILE PROPERTIES

- 8.1. All test specimens shall be cast in a graphite mold in the same heat and in the same manner as the castings which they represent.
- 8.2. Two cast test bars per heat shall be furnished to the purchaser. Bars shall be of sufficient size to be machined into type R3 specimen in accordance with Method 211.1 of Federal Test Method Standard No. 151.
- 8.3. Vendors shall conduct at least two tensile tests per heat.
- 8.4. Tensile tests are to be performed in accordance with Federal Test Method Standard No. 151 using type R3 specimen. Strain rate shall be .005 +/- .002 in/in/min through 0.2 per cent strain.

8. Tensile Properties (continued)

8.5. Tensile properties of each separately cast specimen or specimens sectioned from a critical area of 1A castings shall meet or exceed the following minimum values:

Yield tensile strength (.2% offset)	120,000 psi
Ultimate tensile strength	137,000 psi
Elongation	6 per cent
Reduction of area	10 per cent

9. IDENTIFICATION

9.1. Unless otherwise specified, each casting shall be identified with the part number and an OREMET identification symbol approved by the purchaser by the use of raised numerals in a location indicated on the drawing. When no location is shown on the drawing, the number shall be so located as not to be machined off in finishing to the required casting dimensions. Such numbers shall not be at indicated tool point locations.

10. CHEMICAL REMOVAL OF SURFACE MATERIAL

10. 1. If pickling is specified, all castings shall be pickled to remove .010 inch minimum material per surface. If pickling is not specified, all castings shall be finish-cleaned by pickling to remove .001 to .002 inch material per surface. Foreign material, such as particles of mold, adhering to the casting surface shall be removed prior to pickling. Castings shall not be peened, abrasive blasted or otherwise finished after pickling unless otherwise specified.

11. CERTIFICATION

11.1. Three copies of a quality certification shall accompany or precede each lot of castings. The certification shall include results of analyses in accordance with paragraph 6.2, the results of tensile tests in accordance with paragraphs 8.3 and 8.4, the vendors heat number, the thickness of material removed by pickling in accordance with paragraph 10.1, the quantity of castings constituting that lot, the casting part number, and the purchase order number.

OMC-164-B and OMC-166-A

12. DEFINITIONS

- 12.1. A lot consists of castings of the same heat, the same configuration, the same condition, processed at the same time, and submitted for inspection at the same time.
- 12.2. A heat consists of the material produced in one melting and pouring cycle.

OREGON METALLURGICAL CORPORATION MATERIAL SPECIFICATION OMC-166-A

CASTINGS - TITANIUM, 5-ALUMINUM, $2\frac{1}{2}$ -TIN

1. APPLICABLE SPECIFICATIONS

- 1.1. The following specifications, of the issue in effect on date of invitation bids, form a part of the specification to the extent herein described:
 - 1.1.1. MIL-1-6865 Inspection, Radiographic
 - 1.1.2. MIL-1-6866 Inspection, Penetrant
 - 1.1.3. MIL-C-6021 Castings, Classification and Inspection
 - 1.1.4. Federal Test Method Standard No. 151
 - 1.1.5. X-ray Standards for Titanium Castings (Being prepared)

2. APPLICATIONS

2.1. This specification is primarily for weldable, light-weight, corrosion-resistant, cast parts requiring certified mechanical properties where higher strength is needed than can be obtained from unalloyed titanium castings and better weldability is desired than can be obtained from 6Al-4V alloyed titanium castings.

3. TYPES AND GRADES

3.1. Unless otherwise specified, castings are to be in the ascast condition. If annealed condition is specified, the

3. Types and Grades (continued)

annealing treatment shall be 1500°F for one hour in vacuum, argon, or other atmosphere approved by the purchaser. Dew point of argon shall be no higher than minus 60°F.

4. CASTING METHOD

4.1. When the titanium source is either raw sponge or raw sponge compacts, the sponge shall be double vacuum melted. Use of titanium solids in preparation of electrodes is permitted. The final melting shall be by the vacuum consumable-electrode cold-crucible skull-melt process.

5. COMPOSITION

5.1. Castings shall be of the following composition:

	Weight Per Cent
Aluminum	4.0 - 6.0
Tin	2.0 - 3.0
Carbon	0.1 Max
Nitrogen	0.07 "
Oxygen	0.3
Hydrogen	0.015 "
Iron	0.40
Other Elements (total)	0.30
Titanium	Balance

5.2. Each heat shall be analyzed for each of the elements listed in paragraph 5.1 except titanium. Chemical analysis of each lot shall be certified.

6. QUALITY

- 6.1. Castings shall be uniform in quality and condition, well cleaned, and have a uniformly smooth surface compatible with the casting process.
- 6.2. Unless otherwise specified, metallic grit or shot shall not be used for final cleaning.
- 6.3. The areas of castings subject to soundness requirements shall be as specified and the number and extent of defects

6. Quality (continued)

in such areas shall not be greater than indicated by the standard furnished or approved by the purchaser. Combinations of cracks, shrinkage cavities, cold shuts, or misruns, or other defects not individually cause for rejection, but which are so aligned as to cause stress concentrations are cause for rejection.

6.4. When soundness is specified in accordance with paragraph 6.3 it shall be determined in accordance with visual, penetrant, and radiographic inspection methods established by MIL-C-6021, MIL-1-6865, and MIL-1-6866.

7. TENSILE PROPERTIES

- 7.1. All test specimens shall be cast in a graphite mold in the same heat and in the same manner as the castings which they represent.
- 7.2. Two cast test bars per heat shall be furnished to the purchaser. Bars shall be of sufficient size to be machined into type R-3 specimens in accordance with Method 211.1 of Federal Test Method Standard No. 151.
- 7.3. OREMET shall conduct at least two tensile tests per heat.
- 7.4. Tensile tests shall be performed in accordance with Federal Test Method Standard No. 151 using type R-3 specimens. Strain rate shall be 0.005 +/- 0.002 in/in/min. through 0.2 per cent strain.
- 7.5. Tensile properties of separately cast specimens or specimens sectioned from critical areas of 1-A castings shall meet or exceed the following minimum values:

Tensile Yield Strength (0.2% offset) 105,000 psi Ultimate Tensile Strength 115,000 psi Elongation in 4D 10 per cent

8. IDENTIFICATION

8.1. Unless otherwise specified, each casting shall be identified with the part number and an OREMET identification symbol by the use of raised numbers in a location indicated on the drawing. When no location is shown on the drawing, the

OMC-166-A and OMC-167-T

8. Identification (continued)

number shall be so located as not to be machined off in finishing to the required casting dimensions. Such numbers shall not be at indicated tool locations.

9. CERTIFICATION

9.1. Three copies of a quality certification shall accompany or precede each lot of castings. The certification shall include results of analyses in accordance with paragraph 5.2, the results of the tensile test in accordance with paragraphs 7.3 and 7.4, the OREMET heat number, the quantity of castings constituting that lot, the casting part number, and the purchase order number.

10. DEFINITIONS

- 10.1. A lot consists of castings of the same heat, the same configuration, the same condition, processed at the same time, and submitted for inspection at the same time.
- 10.2. A heat consists of the material produced in one melting and pouring cycle.

OREGON METALLURGICAL CORPORATION TENTATIVE MATERIAL SPECIFICATION OMC-167-T

CASTINGS - TITANIUM ALLOY - HIGH STRENGTH Al - Zr - Sn - Fe - Cr - V

1. APPLICABLE SPECIFICATIONS

- 1.1. The following specifications of the issue in effect on date of invitations to bids form a part of this specification to the extent herein described:
 - 1.1.1. MIL-1-6865: Inspection Radiographic
 - 1.1.2. MIL-1-6866: Inspection Penetrant
 - 1.1.3. MIL-C-6021: Castings, classification and inspection

- 1. Applicable Specifications (continued)
 - 1.1.4. Federal Test Methods Standard No. 151
 - 1.1.5. X-ray Standards for Titanium Castings (Being prepared)

2. APPLICATIONS

2.1. This specification is primarily for light-weight corrosion resistant parts of the highest strength obtainable in cast titanium.

3. TYPES AND GRADES

- 3.1. Unless otherwise specified, castings are to be in the ascast condition. If annealed condition is specified, the annealing treatment shall be 1000°F for four hours followed by air cooling.
- 3.2. Casting classification shall be as specified in the applicable casting drawing. Class definitions shall be as specified in MIL-C-6021.

4. CASTING METHOD

- 4.1. Casting molds shall be rammed graphite mixed with suitable binder unless otherwise specified.
- 4.2. When the titanium source is either raw sponge or raw sponge compacts, the sponge shall be double vacuum melted. Use of titanium solids in preparation of electrodes is permitted. The final melting shall be by the vacuum consumable-electrode cold-crucible skull-melt process.

5. COMPOSITION

5.1. Castings shall be of the following composition:

	Weight Per Cent
Carbon	0.10 Max
Hydrogen	0.015 "
Nitrogen	0.07
Oxygen	0.25 "
Iron	0.5 - 1.5
Aluminum	3.0 - 5.0
Tin	3.0 - 5.0
Zirconium	7.0 - 9.0
Vanadium	0.5 - 1.5
Chromium	0.5 - 1.5
Other Elements (Total)	0.4 Max
Titanium	Balance

5.2. Each heat shall be analyzed for each of the elements listed in paragraph 5.1 except titanium. Chemical analysis of each lot shall be certified.

6. QUALITY

- 6.1. Castings shall be uniform in quality and condition, well cleaned, and have a uniformly smooth surface compatible with the casting process.
- 6.2. Unless otherwise specified, metallic grit or shot shall not be used for final cleaning.
- 6.3. The areas of castings subject to soundness requirements shall be as specified and the number and extent of defects in such areas shall not be greater than indicated by the standard furnished or approved by the purchaser. Combinations of cracks, shrinkage cavities, cold shuts, or misruns, or other defects not individually cause for rejection, but which are so aligned as to cause stress concentrations are grounds for rejection.
- 6.4. When soundness is specified in accordance with paragraph 6.3 it shall be determined in accordance with visual,

6. Quality (continued)

penetrant, and radiographic inspection methods established by MIL-C-6021, MIL-1-6865, and MIL-1-6866.

7. TENSILE PROPERTIES

- 7.1. All test specimens shall be cast in a graphic mold in the same heat and in the same manner as the castings which they represent.
- 7.2. Two test bars per heat shall be furnished to the purchaser. Bars shall be of sufficient size to be machined into type R-3 specimens in accordance with Method 211.1 of Federal Test Method Standard 151.
- 7.3. OREMET shall conduct at least two tensile tests per heat.
- 7.4. Tensile tests shall be performed in accordance with Federal Test Method Standard No. 151 using Type R-3 specimens. Strain rate shall be 0.005 +/- 0.002 in/in/min. through 0.2 per cent strain.
- 7.5. Tensile properties of separately cast specimens or specimens cut from critical areas of 1A castings shall meet or exceed the following minimum values:

Tensile Yield Strength 130,000 psi Ultimate Tensile Strength 150,000 psi Elongation in 4D 6 per cent Reduction in Area 10 per cent

8. IDENTIFICATION

8.1. Unless otherwise specified, each casting shall be identified with the part number and an OREMET identification symbol by the use of raised number in a location on the drawing. When no location is shown on the drawing, the number shall be so located as not to be machined off in finishing to the required casting dimensions. Such numbers shall not be at indicated tool locations.

OMC-167-T and OMC-168-T

9. CERTIFICATION

9.1. Three copies of a quality certification shall accompany or precede each lot of castings. The certificate shall include results of analyses in accordance with paragraph 5.2, the results of tensile tests in accordance with paragraphs 7.3 and 7.4, the OREMET heat number, the quantity of castings constituting that lot, the casting part number, and the purchase order number.

10. DEFINITIONS

- 10.1. A lot consists of castings of the same heat, the same configuration, the same condition, processed at the same time, and submitted for inspection at the same time.
- 10.2. A heat consists of the material produced in one melting and pouring cycle.

OREGON METALLURGICAL CORPORATION
TENTATIVE MATERIAL SPECIFICATION OMC-168-T

CASTINGS - TITANIUM, 2-COPPER

1. APPLICATION

1.1. This specification is primarily for light-weight, corrosion-resistant cast parts where higher strengths are required than can be obtained from unalloyed titanium castings and greater ductility is required than can be obtained from titanium 5Al-2½ Sn castings.

2. CASTING METHOD

2.1. When the titanium source is either raw sponge or raw sponge compacts, the sponge shall be double vacuum melted. Use of titanium solids in preparation of electrodes is permitted. The final melting shall be by the vacuum consumable-electrode cold-crucible skull-melt process.

3. COMPOSITION

3.1. Castings shall be of the following composition:

	Weight Per Cent
Copper	1.0 - 3.0
Carbon	0.10 Max
Nitrogen	0.07
Oxygen	0.25 "
Hydrogen	0.015 "
Iron	0.30 "
Other Elements (Total)	0.40 "
Titanium	Balance

3.2. Each heat shall be analyzed for each of the elements listed in paragraph 3.1 except titanium. Chemical analysis of each heat shall be certified.

4. QUALITY

- 4.1. Castings shall be uniform in quality and condition, well cleaned and have a uniformly smooth surface compatible with the casting process.
- 4.2. Unless otherwise specified, metallic shot or grit shall not be used for final cleaning.
- 4.3. Casting shall be dye penetrant inspected.

5. TENSILE PROPERTIES

- 5.1. All test specimens shall be cast in a graphite mold in the same heat and in the same manner as the castings which they represent.
- 5.2. Two test bars per heat shall be furnished to the purchaser. Bars shall be of sufficient size to be machined into type R-3 specimens in accordance with method 211.1 of Federal Test Method Standard No. 151.
- 5.3. OREMET shall conduct at least two tensile tests per heat.

5. Tensile Properties (continued)

- 5.4. Tensile tests shall be performed in accordance with Federal Test Method Standard No. 151 using Type R-3 specimens. Strain rate shall be 0.005 +/- 0.002 in/in/min through 0.2 per cent strain.
- 5.5. Tensile properties of separately cast specimens shall meet or exceed the following minimum values:

Tensile Yield (0.2% offset)	60,000 psi
Ultimate Tensile Strength	75,000 psi
Elongation in 4 D	12 per cent
Reduction in Area	20 per cent

6. IDENTIFICATION

6.1. If specified, each casting shall be identified with the part number and an OREMET identification symbol by the use of raised numbers in a location indicated on the drawing. When no location is shown on the drawing, the number shall be located as not to be machined off in finishing to the required casting dimensions. Such numbers shall not be at indicated tool point locations.

7. CERTIFICATION

7.1. Three copies of a quality certification shall accompany or precede each lot of castings. The certification shall include results of analyses in accordance with paragraph 3.2 and the results of tensile tests in accordance with paragraphs 5.3 and 5.4, the OREMET heat number, the quantity of castings constituting that lot, the casting part number, and the purchase order number.

8. DEFINITIONS

- 8.1. A lot shall consist of castings of the same heat, the same configuration, the same condition, processed at the same time and submitted for inspection at the same time.
- 8.2. A heat consists of the material produced in one melting and pouring cycle.

REFERENCES

- 1. "Oremet Sees Growing Profit in Titanium Castings", American Metal Market (February 3, 1965), p 7 (RSIC 0026).
- 2. Gleekman, L. W., "The Development, Metallurgy and Corrosion Behavior of Cast Titanium", presented at AIChE Symposium, "The Use of Advanced Metals in the Processing Industries" (September 20, 1964) (RSIC 0028).
- 3. Carter, R. V., "Development of Titanium Alloy Casting Method", AMC Technical Report 60-7-656, September 1960, Aero-Space Division, Boeing Airplane Company, Final Technical Engineering Report, Contract No. AF (600)-36450 (March, 1958, to May, 1960) (RSIC 0024).
- 4. Hardy, R. G., Shaped Titanium Castings, Transactions of Vacuum Metallurgical Conference, Interscience Publishers, New York, 1960, pp 83-98 (RSIC 0174).
- 5. Simmons, D. C., Oregon Metallurgical Corporation, private communication, April, 1965 (RSIC 1116).
- 6. Wood, Nat, "Titanium Castings Enjoy Growing Market", Foundry, 93 (4), 66-69 (April, 1965) (RSIC 0167).
- 7. Ausmus, S. L. and Beall, R. A., "Expendable Casting Molds for Reactive Metals", U. S. Department of Interior, Bureau of Mines, Washington, D. C. RI 6509 (1964) (RSIC 0029).
- 8. "New Deal for Titanium", Chemical Week, <u>88</u> (9), 29, 30, 32 (March 4, 1961) (RSIC 1117).
- 9. Field, A. L., Jr., "Expendable Molds for Titanium Castings", Metal Progress, 70, 92-96 (October, 1956) (RSIC 0388).

- 10. Smith, J. W. and Hamm, T. A., "Factors Contributing to Soundness of Titanium Castings", Trans. AFS, 68, 337-346, 830 (1960) (RSIC 0027).
- 11. Millway, E. E., "Titanium Its Corrosion Behavior and Passivation", Materials Protection, 4 (1), 16-21 (January, 1965) (RSIC 0032).
- 12. "Titanium 1965", a talk given by Ward Minkler of Titanium Metals Corporation of America before the Columbus, Ohio, Chapter of the American Society of Metals, May 5, 1965 (RSIC 1119).
- 13. Elliott, J. F. and Gleiser, M., Thermochemistry for Steelmaking Vol I, Addison-Wesley Publishing Co., Inc., Reading, Mass. (RSIC 0551).
- 14. Margolin, H. and Nielsen, J. P., "Titanium Metallurgy", Modern Materials, Vol 2, H. H. Hausner (Editor), Academic Press, Inc., New York, 1960, pp 225-325 (RSIC 0784).
- Dean, R. S., Long, J. R., Wartman, F. S., and Anderson,
 E. L., "Preparation and Properties of Ductile Titanium", Technical Publication (1961), 13 pp; Metals Technology, 13 (2)
 (February, 1946) (RSIC 0545).
- Dean, R. S., Long, J. R., Wartman, F. S., and Hayes, E. T., "Ductile Titanium Its Fabrication and Physical Properties", Technical Publication (1965), 17 pp; Metals Technology, 13 (2) (February, 1946) (RSIC 0552).
- 17. McQuillan, A. D. and McQuillan, M. K., <u>Titanium</u>, Academic Press, Inc., New York, 1956 (RSIC 0600).
- Kroll, W. J., "Titanium", Metal Industry, 63-66 (July 22, 1955);
 83-86 (July 29, 1955); 105-108 (August 5, 1955); 130-134
 (August 12, 1955); 147-149 (August 19, 1955); 173-174 (August 26, 1955) (RSIC 0594).
- 19. Kroll, W. J., "The Present State of Titanium Extractive Metallurgy", Trans. Met. Soc. AIME, 215 (4), 546-553 (August, 1959) (RSIC 0571).

- 20. Holst, R. and Proft, R., "Über ein Verfahren zur Herstellung von Titanschwamm aus Titantetrachlorid mit Magnesium im Vakuum", Neue Hütte 4 (2), 106-109 (February, 1959) (RSIC 0603).
- 21. Cook, M., "The New Metal Titanium", J. Inst. Metals, 82, 93-106 (1953 to 1954) (RSIC 0604).
- 22. Nowotny, H., Balduin, H., and Piffl, L., "Ein Beitrag Zur Metallurgie des Titans", Metall, 14 (1), 6-11 (January, 1960) (RSIC 0605).
- 23. Jamrack, W. D., Rare Metal Extraction by Chemical Engineering Techniques, Macmillan Co., New York, 1963 (RSIC 0532).
- 24. Miller, G. L., "Production of the Powders of Some of the Reactive Metals", Powder Metallurgy (1/2), 53-64 (1958) (RSIC 0597).
- 25. Opie, W. R. and Moles, O. W., "A Basket Cathode Electrolytic Cell for the Production of Titanium Metal", Trans. Met. Soc. AIME, 218 (4), 646-649 (August, 1960) (RSIC 0572).
- 26. U. S. Patent 2, 892, 697, "Method of Producing Powdered Titanium and Titanium Alloys", G. F. Davies and H. W. Dodds to Clevite Corporation (April 19, 1954) (RSIC 0599).
- 27. Biryukova, L. V., Neroslavskaya, L. L., and Mekhova, E. V., "Specific Surface of Titanium Sponge" (In Russian), Con. Bur. Translation from Zhurnal Prikladnoi Khimii, 33 (12), 2791-2793 (December, 1960) (RSIC 0593).
- 28. Globus, A. R., <u>Titanium Metal Powder</u>, Vantage Press, Inc., New York, 1963 (RSIC 0607).
- 29. Dushman, S., Scientific Foundations of Vacuum Technique, John Wiley & Sons, Inc., New York, 1962 (RSIC 0608).
- 30. Rogers, S. E., "Some Problems in the Powder Metallurgy of Titanium", Powder Metallurgy (7), 249-267 (1961) (RSIC 0547).
- 31. Private communication from Clevite Corporation personnel (RSIC 0609).

- 32. Bunshah, R. F., Margolin, H., and Cadoff, I. B., "Titanium Powder Metallurgy", Precision Metal Molding, 14 (5), 38-40, 67 (May, 1956); 14 (6), 42-43, 137, 138 (June, 1956); 14 (7), 41, 42, 44, 73 (July, 1956) (RSIC 0569).
- 33. Robins, D. A., "The Powder Metallurgy of Titanium", Light Metals, 19 (215), 60-63 (February, 1956) (RSIC 0568).
- 34. Silbereisen, H., "Vorgänge bei der Verdichtung metallischer Pulver zu komplizierten Formkorpern", Planseeberichte für Pulvermetallurgie, 7, 67-78 (1959) (RSIC 0549).
- 35. Kuczynski, G. C. and Zaplatynskj, I., "Density Distribution in Metal Powder Compacts", Trans. AIME, 8 (2), 215 (February, 1956) (RSIC 0610).
- 36. Hoeganaes Sponge Iron Corporation, Iron Powder Handbook (RSIC 0611).
- 37. Taylor, H. G., "The Influence of Tooling Methods on the Density Distribution in Complex Metal-Powder Parts", Powder Metallurgy (6), 87-128 (1960) (RSIC 0612).
- 38. Oakley, J., "Some Development in Metal Powder Presses", Powder Metallurgy (6), 1-19 (1960) (RSIC 0601).
- 39. Schwope, A. D., "Titanium and Zirconium Powder Metallurgy", Powder Metallurgy, W. Leszynski (Editor), Interscience, New York, 1961, pp 731-745 (RSIC 0534).
- 40. Robins, D. A., Pitkin, W. R., and Jenkins, I., "Preparation and Properties of Titanium and Titanium Alloys Prepared by Sintering", Symposium on Powder Metallurgy, Iron and Steel Institute Special Report No. 58, 1956, pp 264-271 (RSIC 0539).
- 41. Weber, E. P., "High Strength Sintered Parts Made from Titanium Powder", Progress in Powder Metallurgy, 17, 19-28 MPIF (1961) (RSIC 0536).
- 42. Onitsch-Modl, E. M., "Zur Pulvermetallurgie der Leichtmetalle", Berg-und Huttenmannische Monatshefte, 101 (12), 363-369 (1956) (RSIC 0546).

- 43. Mints, R. S., "Kinetics of the Sintering of Metal Powders" (In Russian), Russian Journal of Inorganic Chemistry, <u>5</u> (4) (April, 1960) (RSIC 0598).
- 44. Powell, R. A., "Cyclic Sintering of Metals", MPIF 20th Conference Proceedings (1964), pp 139-144 (RSIC 0558).
- 45. Chang, W. H., "A Dew Point-Temperature Diagram for Metal-to-Metal Oxide Equilibria in Hydrogen Atmospheres", J. Am. Welding Soc., 35 (12), 622s-624s (December, 1956) (RSIC 0613).
- 46. Wile, G. J., "Titanium Parts Made by Powder Metallurgy Methods", Materials and Methods, 49 (1), 95-97 (July, 1956) (RSIC 0555).
- 47. Dodds, H. W., "A Fabricator Views Titanium Powder Metallurgy", Proc. Eleventh Annual Meeting Metal Powder Association, Philadelphia (May, 1955), pp 108-113 (RSIC 0573).
- 48. Weber, E. P., "A Short Cut to Titanium Parts", Modern Metals, 13 (1), 48-50, 52 (1957) (RSIC 0556).
- 49. Dodds, H. W. and Davies, G. F., "Hot Pressing, Press Forming Loom as Answers to Titanium Fabrication", J. Metals, <u>6</u> (10), 1116-1118 (October, 1964) (RSIC 0570).
- 50. Jackson, H. C., "Isostatic Pressing of Powdered Materials", Progress in Powder Metallurgy 1964, MPIF-APMI (1964), pp 159-167 (RSIC 0602).
- 51. Jackson, H. C., "Isostatic Pressing Extends Horizon of Powder Metallurgy", Machinery, 70 (8), 126-129 (April, 1964) (RSIC 0548).
- 52. Hodge, E. S., Boyer, C. B., and Orcutt, F. D., "Gas Pressure Bonding", Ind. Engr. Chem., <u>54</u> (1), 30-35 (January, 1962) (RSIC 0614).
- 53. Powell, R. A., "Isostatic Compaction of Metal Powders in Conventional Molding Tools", Frankford Arsenal Memorandum Report M65-2-1 (July, 1964) (RSIC 0137).

- 54. Bunshah, R. F. and Juntz, R. S., "Isostatic Compaction of Pure Metals Without Contamination", University of California, Lawrence Radiation Laboratory Report UCRL-6932 on Contract No. W-7405-eng-48 (January 18, 1963) (RSIC 0550).
- 55. Franssen, H. and Franssen, N., "Überblick über den derzeitigen Stand des Pulverwalzverfahrens", Zeits fur Metallkunde, 53 (2), 78-85 (February, 1962) (RSIC 0553).
- 56. Evans, P. and Smith, G. C., "Some Preliminary Experiments on the Continuous Compaction of Titanium, Molybdenum, and Tungsten", Metallurgia, 59, 117-120 (March, 1959) (RSIC 0554).
- 57. Tikhonov, G. F., Sorokin, U. K., and Khromov, V. G., "Rolling Highly Porous Strip for Filters of Titanium Powder", Trudy Leningradskogo Politekhnicheskogo Instituta imini M. I. Kalinina, 222, 71-72 (1963); Translation: JPRS 23,596 (March 10, 1964) (RSIC 0125).
- 58. Aksenov, G. I., Khromov, V. G., Nikolayev, A. N., and Semenov, Yu. N., "Rolling Titanium Powder into Thin Strip by the Gorkiy Polytechnic Institute Method", Titan i yego splavy, metallovedeniye titana, Academy of Sciences Publishing House, Moscow, 3, 152-158 (1960) (RSIC 0135).
- 59. Long, J. R. and Hayes, E. T., "Sheath Working of Metal Powders, U. S. Bureau of Mines Report of Investigations: R. I. 4464 (February, 1949) (RSIC 0557).
- 60. Williams, J., "The Consolidation of Metal Powders by Hot Working Within Sheaths", Powder Metallurgy, 94-103 (RSIC 0615).
- 61. Hagemeyer, J. W., "Powder Compaction by High Velocity Impact", communication from General Dynamics/Fort Worth Laboratories (January 15, 1964) (RSIC 0528).
- 62. Geltman, G., "Explosive Compacting of Metal Powders", Progress in Powder Metallurgy, 18, 7-13 (1962) (RSIC 0527).
- 63. Hausner, H. H., "Compacting and Sintering of Metal Powders Without the Applicability of Pressure", Agglomeration, Intersciences (1962), pp 55-88 (RSIC 0531).
- 64. Montgomery, W. T., "The Compacting of Metal Powders by Explosives", Powder Metallurgy (6), 125-128 (1960) (RSIC 0526).

- 65. Gorbunev, N. S., Shatalova, I. G., Likhtman, V. I., and Rebinder, P. A., "An Investigation of the Principles in Vibration Pressing of Powder Metal Materials". Issledovaniya po Zhareprochnym Splavam, 8, 103-110 (1962); Translation: JPRS 16, 269 (November 20, 1962) (N63-10579) (RSIC 0121).
- 66. Borok, B. A., Golubev, L. S., Shchegolev, R. P., and Ruch'eva, "Mechanical Properties and Microstructure of Sintered Titanium Alloys", Translation from Poroshkovaya Metallurgiya, 15 (3), 88-98 (May to June, 1963) (RSIC 0540).
- 67. Grimwade, M. F., "Titanium-Aluminum-Manganese Alloys Prepared by Powder Metallurgical Techniques", Powder Metallurgy (7), 283-295 (1961) (RSIC 0537).
- 68. Gooding, R. W. and Parratt, N. J., "Solid Titanium Nitride and Other Refractory Compounds Made by Direct Gas/Metal Reaction", Powder Metallurgy (11), 42-58 (1963) (RSIC 0538).
- 69. Smart, R. F. and Ellwood, E. C., "The Powder Metallurgy of Titanium-Tin Alloys Containing up to 15% Tin", Powder Metallurgy (4), 108-119 (1959) (RSIC 0535).
- 70. Kuhn, W. E., Kinsey, H. V., and Ellis, O. W., "A Study of Some Alloys of Titanium", Canadian Mining and Metallurgical Bulletin, 43 (454), 74-87 (February, 1950) (RSIC 0533).
- 71. Larsen, E. I., Swazy, E. F., Busch, L. S., and Freyer, R. H., "Properties of Binary Sintered and Rolled Titanium Alloys", Metal Progress, 55, 359-361 (March, 1949) (RSIC 0541).
- 72. Bokok, B. A., Golubev, L. S., and Shchegolev, R. P., "Effect of Heat Treatment on the Structure and Properties of Titanium Alloys", Titan i Yego Splavy, Metallovedeniye titana, 3, 10-16 (1960); Translation: JPRS 17, 155 (January 16, 1963) (N63-11872) (RSIC 0133).
- 73. Kornilov, I. I., Mikheyev, V. S., et al., "Effect of Aluminum on the Structure and Properties of a Six-Component Powder Metallurgy Alloy of the Ti-Al-Cr-Fe-Si-B System", Titan i Yego Splavy, Metallokhimiya i Novyye Splavy, 7, 130-134 (1962); Translation: JPRS 15,909 (October 29, 1962) (N62-17761) (RSIC 0122).

- 74. Kornilov, I. I., Pylayega, Ye. N., et al., "Effect of Silicon on the Structure and Properties of a Six-Component Powder Metallurgy Alloy of the Ti-Al-Cr-Fe-Si-B System", Titan i Yego Splavy, Metallokhimiya i Novyye Splavy, 7, 135-139 (1962); Translation: JPRS 15,909 (October 29, 1962) (N62-17761) (RSIC 0123).
- 75. Timoshenko, N. N. and Petunin, Ye. V., "Investigation of the Microstructure and Mechanical Properties of Alloys of Titanium with Aluminum", Titan i Yego Splavy, Metalloredeniye Titana, 3, 3-9 (1960); Translation: JPRS 17, 155 (January 16, 1963) (N63-11872) (RSIC 0132).
- 76. Shchegolev, R. P. and Golubev, L. S., "Powder Metal Alloys with High Strength", Titan i Yego Splavy, Metallovedeniye Titana, 3, 84-89 (1960); Translation: JPRS 17, 155 (January 16, 1963) (N63-11872) (RSIC 0134).
- 77. Jech, R. W. and Weber, G. P., "Development of Titanium Alloys for Elevated Temperature Service by Powder Metallurgical Techniques", Final Report on Navy Contract No. NOas 55-953-C (July 15, 1957) (RSIC 0616).
- 78. Jech, R. W., Schwope, A. D., and Weber, E. P., "The Development of SAP-Type Structures in Titanium for Elevated Temperature Service by Powder Metallurgical Techniques", High Temperature Materials, John Wiley & Sons, Inc., New York, 1959, pp 332-341 (RSIC 0521).
- 79. Jech, R. W., Weber, E. P., and Schwope, A. D., "Fiber-Reinforced Titanium Alloys", Reactive Metals, Interscience, New York, 1959, pp 109-116 (RSIC 0529).
- 80. Price, D. E. and Wagner, H. J., "Preparation and Properties of Fiber-Reinforced Structural Materials", DMIC Memorandum 176 (August 22, 1963) (RSIC 0617).
- 81. Jacobson, M., Cooper, A. R., and Nagy, J., "Explosibility of Metal Powders", U. S. Bureau of Mines Report of Investigation: RI 6516 (1964) (RSIC 0522).
- 82. Mash, Donald R., "Plasma-Arc Spraying of Space-Age Materials", Metals Engineering Quarterly, Vol 2, November 1962, pp 1-8 (RSIC 0479).

- 83. Levinstein, M. A., "Properties of Plasma-Sprayed Materials", WADD Technical Report 60-654, Contract No. AF 33(616)-6376 (January, 1961) (RSIC 0519).
- 84. Levinstein, M. A., "Properties of Plasma-Sprayed Materials", Technical Documentary Report No. ASD-IDR-62-201, Contract No. AF 33(616)-6376 (June, 1962) (RSIC 0520).
- 85. Stanton, W. E., "Metal Spraying Under Protective Atmospheres", Engineers Digest (London), 20 (11), 445-447 (1959) (RSIC 0477).
- 86. Cowden, L. M., Linde Company, Division of Union Carbide Corporation, Indianapolis, Indiana, personal contact (RSIC 1120).
- 87. Ingham, H. S., Jr., Metco Incorporated, Westbury, Long Island, New York, personal contact (RSIC 1121).
- 88. Unger, R., Giannini Plasmadyne Corporation, Santa Ana, California (RSIC 1122).
- 89. Garrabrant, E., Linde Development Laboratories, Newark, New Jersey (RSIC 1123).
- 90. Ingham, H. S., Jr., "Some Advances in Combustion and Plasma Flame Spray Coatings", Presentation to Ninth Meeting of the Refractory Composites Working Group, Worcester, Massachusetts (August, 1964) (RSIC 0478).
- 91. Safranek, W. H., "A Survey of Electroforming for Fabricating Structures", RSIC Report 210 (August, 1964) (RSIC 0743).
- 92. Stetson, A. R., "Titanium Coatings Protect Metals", Materials Engineering and Design (March, 1963) (RSIC 1124).
- 93. Titanium Metallurgical Laboratory Memorandum, "Status of Electroplated Titanium Coatings on Other Metals and Electroformed Titanium" (August 30, 1957) (RSIC 1125).
- 94. Private communication from S. Senderoff (RSIC 1126).
- 95. Private communication from D. K. Baker (RSIC 1127).
- 96. "Chemical Vapor Deposition", DMIC Report 170 (June 4, 1962) (RSIC 0816).
- 97. Powell, C. F., Oxley, J. H., and Blocher, J. M., Jr., Vapor Deposition, John Wiley & Sons, Inc., New York, 1965 (RSIC 0817).

THE MAKING OF TITANIUM AND TITANIUM-ALLOY SHAPES BY CASTING, POWDER METALLURGY, AND OTHER PROCESSES

By J. G. Kura, V. D. Barth, H. McCurdy, W. H. Safranek, E. H. Hall, and H. O. McIntire

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

W. A. WILSON

Chief, Methods Development Branch

J. PXORR

Chief, Manufacturing Research and

Technology Division

WERNER R. KUERS

White

Director, Manufacturing Engineering

Laboratory